A SHORT TEXT-BOOK OF INORGANIC CHEMISTRY

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EDITOR'S PREFACE.

ALTHOUGH the number of short Text-books of Inorganic Chemistry is large, it is hoped that this little book will supply a definite want among teachers and students, corresponding to that which the Editor has himself felt.

The principles which have guided the Author in writing the book are fully stated in his Preface, and with these the Editor entirely concurs ; but in adapting the book for English students certain alterations and additions were necessary, and to these the Author has given his full consent.

The whole book has been carefully revised throughout, and the physical constants brought up to date. Considerable additions have been made to the descriptions of water, atmospheric air, coal, iron, &c. Short accounts of Gay-Lussac's law, Avogadro's law, and the manufacture of coal-gas have also been introduced into the text.

In the Appendix, which is entirely new, a brief account has been given of the methods used for determining atomic and

molecular weights, of Prout's law, and of the Periodic law. The Editor acknowledges his indebtedness to Lothar Meyer's 'Moderne Chemie' in writing this Appendix. Finally, a series of tables has also been added, which it was thought would prove useful in the laboratory. Some of these have been taken from Landolt and Börnstein's excellent collection of physical tables.

The range which the book covers is rather more than that required for the Intermediate Science and Preliminary Scientific (M.B.) Examinations of the London University, and the needs of students working for these examinations have been steadily kept in view, but without following the syllabus in a servile manner.

ABERYSTWYTH: *March*, 1884.

AUTHOR'S PREFACE.

THIS short Text-book has been written to recall to the memory of students who have attended a course of lectures on Experimental Chemistry what they have seen and heard, and to clear up any points which may not have been properly understood.

A necessary condition for using a text-book of chemistry successfully is attentive and continuous attendance at the lectures. Students in arts who have not regularly attended a course of lectures may be able to read up afterwards what they have missed; but a lecture which has not been attended by a student of chemistry cannot be made up by mere reading—neither the notes of the lecture by other students, which ought to be extremely few, nor a text-book, can serve as a substitute for what has not been heard. The chemist has to learn, not by reading nor by hearing alone, but both by hearing and seeing. A person who has not *seen* the phenomena produced by the union of oxygen and hydrogen, for example, can have no clear conception of them, nor of the chemical change which accompanies them. Nothing is more foolish than the opinion, which

I have often heard from young medical students, that chemistry can be studied from books alone, like other subjects; that facts which are learnt by heart can take the place of general principles only partially understood.

The opinion of chemists as to how many of the immense number of empirical facts now known in chemistry should be introduced into lectures appears to be very different. I quite agree with Fittig when he says: 'Chemistry can no longer be taught as a descriptive science; in lectures on chemistry the general nature and principles of chemical phenomena should take the first place, and should be illustrated by experiments, but all the many compounds should not be enumerated and described.' But my opinion differs from that of Fittig when he, rather inconsistently, goes on to add: 'But in teaching chemistry in this manner it is still requisite to offer to the student as easily and completely as possible the material on which these general principles are based.'

The study of chemistry is similar to that of a language. What is learnt in the lectures scarcely goes as far as reading and parsing; at most it only includes the rules by which words are built up into sentences. To use the language with success—to speak it—continued practice is required.

The same is also true of chemistry: the science is learnt in the laboratory, not in the lecture theatre. The most that can be done in the lectures is to prepare the student for successful work in the laboratory.

And although teachers in law, history, and philosophy give the best they have in their lectures, experimental chemistry, as taught in the lecture theatre, must be elementary. To enumerate many chemical facts loads the memory with ballast, and tends to learning by rote instead of clear perception and afterthought.

The problem of the lecturer on chemistry is therefore to give his hearers an idea of chemical processes and the most important chemical theories without burdening their memories with a large number of mere facts, and thus to prepare them to acquire an accurate knowledge of chemistry by their own practical work.

I have adhered to this general principle in writing this short Text-book. I have also endeavoured not simply to give a series of dry facts, but to blend them together into one continuous narrative.

Of the students attending chemical lectures, those making chemistry a special study are nearly always in a minority. A complete description of those parts of the science (*e.g.* the rare elements, the ammoniacal compounds of cobalt and the platinum bases) which have only interest for these few and not for those studying medicine, pharmacy, agriculture, &c., is therefore out of place both in lectures and in elementary books; and all the more so as the special study of these subjects is better carried on in the laboratory. Such subjects are therefore briefly treated in this Text-book, while others of general interest, such

as water, atmospheric air, carbon, carbonic acid, arsenious acid, the detection of arsenic in cases of poisoning, salts, iron, lime, &c., are referred to more fully.

The engravings in the text are limited in number: they illustrate only such apparatus as I consider to be especially adapted to recall to the student what he has seen in the lectures.

PREFACE TO THE SECOND EDITION.

THE greater part of the present edition had been revised by Dr. Humpidge last summer, but being unable, owing to failing health, to complete the revision, he requested me to undertake it, and to see the book through the press.

Some notes, intended to form an additional Appendix, were handed to me at the same time: these will be found on pp. 586–588.[1]

In accordance with recent researches, the atomic weight of beryllium has been altered from 13·6 to 9·1; the description of the metal and its compounds has also been transferred to the section treating of the metals of the alkaline earths.

D. E. JONES.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH:
April 1888.

[1] In the third edition these have been placed, in the order of the pages to which they respectively refer, amongst the other notes which may be found on pp. 586–595.

PREFACE TO THE THIRD EDITION.

THE results of researches instituted since this book was written have rendered many alterations and additions imperative.

Where the statements made no longer accorded with the known facts, the necessary alterations have been in most cases at once introduced into the body of the book ; but, in order to save needless expense, additional matter has more frequently been placed amongst the 'Notes' which follow the original appendix. These notes are placed in the order of, and are headed by, the pages to which they respectively refer, and attention is called to them on those pages by the words 'See Appendix' (sometimes contracted to 'See App.').

It is believed that this edition will be found to have been corrected up to date. As some indication of the attempt that has been made to do this, it may perhaps be added that, on an average, about one page in every four has been subjected to more or less alteration, and the notes have been increased from ten in number to sixty-five.

H. LLOYD SNAPE.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH :
November 1891.

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TEXT-BOOK

OF

INORGANIC CHEMISTRY.

INTRODUCTORY.

THE science of Chemistry is closely related to that of Physics, and it is the aim of both sciences to solve nearly the same problems. The province of both is to investigate the processes of nature perceptible to the senses, to discover the course they take, their connection with one another, and their causes, and to investigate the laws according to which the forces of nature act, whatever may be the objects or classes of bodies upon which their action is exerted.

These two sciences—Chemistry and Physics—are the foundation of all other natural sciences—of mineralogy and geology, of zoology and botany, as well as of astronomy, and especially of the whole of medical science, which endeavours to fathom the processes produced in a certain class of bodies by chemical and physical forces.

If we consider what goes on around us in nature, we perceive the change from day to night, we notice the moon and apparently the sun revolving round the earth, as well as similar movements in other heavenly bodies ; we feel the movements of the air, perceive the change of temperature ; we notice water freezing, and admire the rainbow, the thunderstorm, formation of clouds, &c. All these phenomena belong to the processes of physics ; but where shall we, then, *look for chemical processes ?*

Simple chemical processes are not nearly so common in nature as simple physical processes, and this is certainly the reason why physical phenomena and physical laws were investigated many

centuries before any idea of a natural law in chemistry was conceived.

We notice plants growing and animals breathing, both which processes go on by the inter-action of chemical and physical forces. But how plants assimilate the constituents of atmospheric air, and work them up chemically into their substance, still remains a mystery to the chemist and physicist at the present day.

When a tree is struck by lightning and burns, this is certainly a chemical process, and one much simpler than the growth of a plant. But although man has known from time immemorial how to produce fire, and has had the chemical process of burning wood daily before his eyes, a correct explanation of a process apparently so simple was only obtained at the end of the preceding century. For this reason chemistry may well be called the younger sister of physics.

The intelligent observer also perceives numerous other chemical processes going on in nature; he notices the weathering of rocks, the putrefaction of animal and vegetable matter, the deposition of limestone in caverns, the rusting of iron, the souring of milk, wine, &c.; but these and similar changes usually go on so slowly that their progress is difficult to follow.

Innumerable chemical processes were introduced by man thousands of years ago. It was found that lime which had lain in the fire—quick-lime—became hot when brought into contact with water, that it possessed generally other properties than the lime which had not been burnt; metals had been extracted from their ores by heating with charcoal; white arsenic had been obtained by roasting other ores; sulphur had been burnt in the air and the suffocating acid gas so produced had been noticed. But these and a hundred other similar changes could only be correctly understood and explained after the common cause of them all—fire—and the process of combustion had been made clear.

For this reason, the discovery of oxygen—of that substance which is as necessary for combustion as it is for respiration—by Priestley and by Scheele, and Lavoisier's first correct explanation of combustion, are the pillars which carry the noble edifice of modern chemistry, based on the foundation of numerous earlier observations.

In what manner, then, do chemical and physical processes differ from one another—which phenomena belong to chemistry and which to physics? The answer may be easily given in a few words,

but will not be so easily understood by those to whom chemical phenomena are strange.

Chemical processes are those by which bodies undergo a material change. In physical processes, pure and simple, the *substances* in which we notice a change remain materially unchanged. But what is to be understood by a material change? This will best be explained by a few examples.

A stick of sulphur when rubbed becomes electric and attracts small pieces of paper or other light bodies, and then repels them. The same sulphur, if heated in a test tube, melts to form a pale yellow, clear liquid, and changes at a higher temperature to a reddish-brown gas, which externally has not the remotest similarity with the solid yellow sulphur. But has the sulphur by the rubbing or by the heating undergone a material change, have *chemical* processes taken place in both cases?

The answer to this question is a negative. The *substance* of the sulphur is the same after the rubbing as before, and sulphur gas, as well as liquid sulphur, have the same relation to solid sulphur as water gas or water vapour, and liquid water to solid water or ice. We have here to do with a change in the state of aggregation produced by heat, which only lasts as long as the cause producing it. Just as water gas by cooling again becomes first liquid water and then solid water, so the sulphur gas changes into liquid sulphur and then into solid sulphur, with exactly the same properties as it possessed at first, as soon as the source of heat is removed.

But something quite different happens when we heat sulphur in an open vessel, so strongly that it catches fire and burns with a blue flame. In this case, too, it changes entirely into a gas, the colourless gas with the well-known odour of burning sulphur. If we cool the gas, for example, by leading it through a vessel surrounded with cold water, we should in vain expect to obtain liquid or solid sulphur from it. By this process the sulphur has suffered a material change—*i.e.* a change which continues after the cause has been removed. The sulphur has united chemically with a constituent of the air, and a new substance has been produced.

If we intimately mix together yellow sulphur and metallic iron, both in the state of a fine powder, we obtain a grey substance, which externally has no similarity with either of the bodies from which it was produced. It might be thought that this grey powder no longer consists of yellow sulphur and black iron, and that the

two substances had undergone a material change by the act of mixing them.

We can, however, readily convince ourselves that this mixture really contains unchanged sulphur and iron. The lighter sulphur may be easily separated by the mechanical process of washing, and the iron may be removed by a magnet—which would not be possible with the product of real chemical action.

Let us prepare a mixture of four parts of sulphur and seven parts of iron, both finely powdered, and heat the mixture in a test-tube in the gas lamp. In a short time that portion of the mass which is most strongly heated commences to glow; the glowing then spreads through the entire mixture, and finally ceases of itself. It seems remarkable that at this high temperature none of the volatile sulphur is given off.

Sulphur and iron, which when only mixed remain chemically unchanged, attract one another chemically when heated to a certain high temperature, and then both of them suffer a material change. The dark-grey, solid, hard product may be easily pulverized, but this powder has now quite different properties to the mere mixture of sulphur and iron. We might try in vain to separate the sulphur by washing or by any other mechanical operation, or to extract the iron by the magnet. Sulphur and iron experience a material change when heated together, and in such a manner that it might be asked whether the new product really contains sulphur and iron, or whether both have not been lost by the operation.

This question cannot be decided *a priori*, nor by mere philosophising, but only by experiment, and it has been so decided.

If the sulphur and the iron had been lost on their union, if they were no longer contained in the compound, it would not be possible in any imaginable manner to again separate them with their original properties. But chemistry teaches that, in this and other cases, compounds may be again decomposed into their constituents, and that the same *quantities* of these constituents may be again obtained. The process of building up a chemical compound from its constituents, as here illustrated in the case of sulphur and iron, is called *synthesis*: the reverse of this is *analysis*.

The union, or, as we may say, the coalescence—of the constituents of a chemical compound is so close that by no means can either of them (*e.g.* the yellow sulphur in the above compound) be perceived in the dust of a compound, not even with the most powerful microscope. It is thus clear why it is impossible to split

up a chemical compound by pure mechanical means. *Substances united by chemical force can be only separated by some force acting chemically.*

Those substances which we cannot further decompose by chemical analysis we call simple bodies, or *elements*, without wishing to assert that they are really undecomposable. They are elementary substances for us only as long as we have not succeeded in decomposing them.

The inquiry after the fundamental substances of inorganic and organic nature is as old as the investigation of nature itself; but what we understand to-day by the word *chemical element* is something quite different from what was formerly so called. The statement of the early philosophers, who neglected experiment and exact investigation, that *Fire*, *Air*, *Water*, and *Earth* were elements, rather meant that all natural bodies *have their origin* in these four things, than that they *consist* of them. And when this question was more critically examined and experimentally investigated, these four elements of the ancients were abandoned.

It is now known that what is called fire is not a substance but a phenomenon; that water consists of two gaseous bodies, as yet incapable of further decomposition, oxygen and hydrogen; that air is a mechanical mixture of two gaseous substances, oxygen and nitrogen; and that earth is no single individual substance, but an agglomerate of thousands of very different chemical elements and compounds.

Our present chemical elements are the result of experiment. Their number is somewhat large, and, according to experience, will probably increase. We already know more than sixty.

When it is considered how easy it is for us to decompose water into its constituents, and to reproduce it from them, the question arises, how was it possible that up to a hundred years ago water was thought to be an elementary substance, how was it possible that one of the many methods which we now know for its decomposition, had not been discovered much earlier?

The principal agent, which was previously almost exclusively employed in order to produce chemical decomposition, was a high temperature, or fire. Crucibles, heating furnaces, distilling apparatus were most indispensable in furnishing the laboratory of an alchemist. If water had possessed the property to be decomposed at a high temperature, its compound nature would have been recognized long previously. That it remains unchanged at a red-

heat could only help to confirm the belief that it was undecomposable. (See Appendix.)

The methods which we now use to decompose water were partly unknown to the chemist of earlier centuries, and were partly wrongly interpreted.

To the former, belong the electrolytic force of the galvanic current, and the action of those metals, only discovered later, which decompose water at the ordinary temperature: potassium, sodium, &c. To those processes by which water is decomposed, and which were long known, but were previously falsely explained, belongs the reaction which occurs when iron is brought into contact with water and a strong acid. Everyone who sees this experiment for the first time believes, as was formerly done, that the gas evolved from the iron is extracted from this metal, whereas it really arises from the decomposition of the water.

Let us consider this and other processes by which water is decomposed more exactly.

If we dip two platinum plates into water which is made slightly acid with sulphuric acid (pure water is a bad conductor of the current), and then connect the plates with the poles of a galvanic battery of four or six Bunsen's cells, we notice at the moment when the circuit is completed that gases are evolved from both platinum plates, and that this evolution continues as long as the galvanic current remains unbroken.

If two small tubes of equal size, filled with water, are placed over the platinum plates, so that the gas evolved from one plate is collected in the one tube, and that evolved from the other plate in the other (fig. 1), we notice the following results:—

i. The gas collecting over the positive electrode [1] regularly fills a smaller space than that collecting over the negative electrode; exact measurements have shown that the volume of the latter is just twice as much as that of the former.

ii. If a lighted body is brought near the gas from the negative pole, when it is allowed to flow out by opening the stopcock, it catches fire and burns with a feebly luminous flame. The gas from the positive pole does not possess this property; it does not burn itself, but it supports the combustion of other bodies in such

[1] The two pieces of platinum which bring the current to the water are called *poles* or *electrodes*. The one which is connected with the zinc of the battery is the *negative* pole or electrode, the other which is attached to the copper, carbon, or platinum of the battery is the *positive* pole or electrode.—ED.

a manner that a glowing chip of wood brought into contact with it at once catches fire and burns with a bright light.

We call the latter gas *oxygen*, the former *hydrogen*. These are the elementary constituents of water, on the re-union of which water again results.

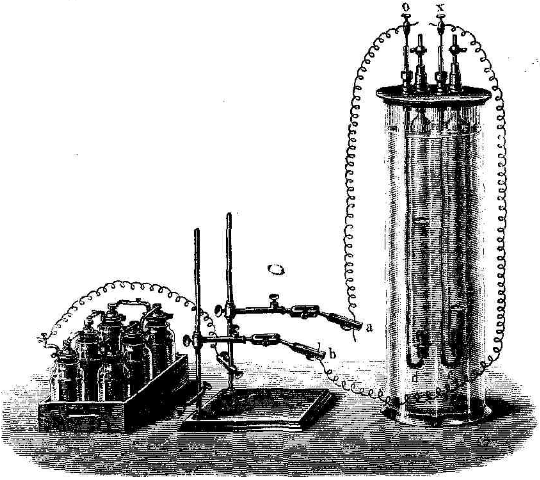

Fig. 1.

We will now consider each of these substances separately. Oxygen may well be taken first, as it belongs to the most widely distributed elements, and since our present scientific chemistry dates from its discovery, with the correct explanation of the processes of combustion which immediately followed.

OXYGEN.

Chemical Symbol: O.—*Atomic Weight*: 16.

Oxygen belongs to those elements which are most widely distributed in nature. The atmosphere contains 23 per cent. of oxygen by weight, water 88·9 per cent., and it is further one of the chief constituents of the innumerable chemical compounds which make up the solid crust of the earth. Oxygen is as widely distributed in organic as in inorganic nature; and it is present in many of the numerous products of animal and vegetable life. Sugar, cellulose, starch, and many other similar bodies, contain more than 50 per cent. of oxygen.

At the first glance it seems almost incredible that a substance so very widely distributed in nature as oxygen, and even occurring in the free state in atmospheric air, should not have been discovered earlier than the end of the preceding century.

The honour of its discovery belongs to two chemists, Priestley and Scheele, who, quite independently of one another, observed and described it in the year 1774.

Oxygen is a gaseous substance which can only be condensed to a liquid when exposed to immense pressure and extreme cold. It was long thought to be only capable of existing in the gaseous state, and was one of the so-called 'permanent gases.' Later experiments showed that, by improved methods of producing a high pressure combined with intense cold, oxygen may be liquefied. It is, *e.g.*, liquefied at $-130°$ under a pressure of 470 atmospheres.

The gas is colourless and transparent, without taste or smell, and may be respired like common air. It is in fact the free oxygen in the air which supports respiration.

Like common air, it is only slightly soluble in water: 100 volumes of water free from air at 4° dissolve only 3·7 volumes of oxygen, or one kilogramme of water dissolves 0·053 gramme of oxygen.

Oxygen is a little heavier than common air; its specific gravity, compared with air as unity, is 1·1056. Since one litre of air at 0°, and under a barometric pressure of 760 mm., weighs 1·293 gramme, one litre of oxygen under similar circumstances weighs 1·429 gramme.

Notwithstanding its immense distribution in nature and its innumerable compounds, only a few substances are adapted for the preparation of oxygen.

We may obtain it from water by electrolysis in the manner just described. But although this method gives very pure oxygen, it is not suited for the preparation of large quantities. Among the numerous minerals containing oxygen very few can serve directly for its preparation. The foremost of these few is pyrolusite, an oxygen compound of a metal—manganese—closely resembling iron. This compound is called by chemists *manganese peroxide* (black oxide of manganese). It is a greyish-black ore which occurs somewhat largely in nature, and possesses the property when heated of parting with a portion of its oxygen, forming another compound of the same metal containing less oxygen.

In order to prepare oxygen from it, a long iron tube, closed at one end, about the size of an ordinary gun-barrel, is filled with small pieces of the broken mineral. The open end is then closed with a cork, pierced to receive a glass tube, and heated in a gas or charcoal furnace. As soon as it commences to become red-hot, gas is freely evolved from the glass tube, which is allowed to dip under water. The gas which is first given off, and which is contaminated with the atmospheric air present in the tube, is allowed to escape; the oxygen may then be collected in glass cylinders or in a gasometer as required.

This method gives large quantities of oxygen easily and quickly, but not of perfect purity. A compound of manganese, containing less oxygen (trimanganic tetroxide), remains behind in the tube, and gives off no further oxygen, even when very strongly heated.

A larger quantity of oxygen may be obtained by heating the mineral with sulphuric acid, but for other reasons this method is not to be recommended.

In order to prepare oxygen from the atmospheric air, the nitrogen, with which it is mechanically mixed, must be removed in the shape of some non-volatile chemical compound. This, however, cannot be done, since the force which produces chemical union, and which we call chemical affinity, is very powerful in the case of oxygen, and the reverse in that of nitrogen; in consequence of this, nearly all attempts to fix the nitrogen of the air in a chemical compound result in binding the oxygen, while the nitrogen remains free.

We can, however, accomplish our purpose in a roundabout way. We can cause the oxygen of the air to unite with some other body, producing a compound, which, like the pyrolusite, again gives up its oxygen under favourable circumstances. This may be done in the following manner.

The metal mercury possesses the property of combining chemically with the oxygen of the air, when heated up to a certain temperature (320°), which must not be exceeded to any great extent. By this process it loses its metallic lustre, and becomes changed into a red powder, called red oxide of mercury (mercuric oxide). This product has the remarkable property of decomposing into its constituents—mercury and oxygen—when heated to a

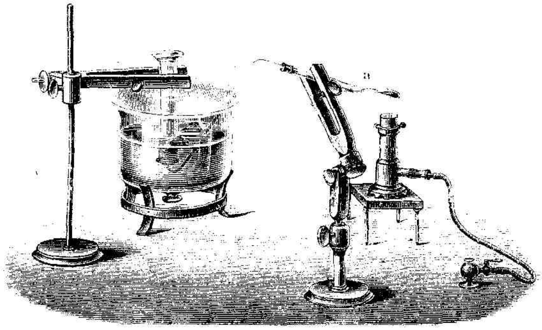

Fig. 2.

temperature a little higher than that necessary for its production. In this way, which was first used by Priestley to prepare the gas, oxygen may be indirectly obtained from the air, in a state of great purity.

The accompanying figure (fig. 2), shows a simple apparatus for the preparation of oxygen from this mercuric oxide, which may be also used to determine the quantity of mercury by weight contained in the weighed quantity of mercuric oxide employed. The mercuric oxide is contained in the closed end of the tube of difficultly-fusible glass, as shown in the figure. Its weight is determined by weighing the bent tube when empty, and then again

when the substance has been introduced ; the difference in weight gives the quantity of mercuric oxide employed. A cork with a bent glass tube is then fitted air-tight in the open end, its other end dipping under a cylinder filled with water. If the mercuric oxide is now heated by a gas flame, and the heating continued until it has all vanished, the oxygen which was previously present in it passes over into the glass cylinder standing over water, and the less volatile mercury is deposited in the cooler portions, *a*, of the tube.

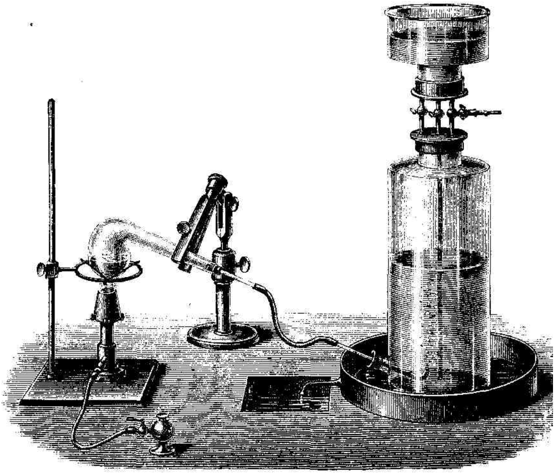

Fig. 3.

If the tube containing the metallic mercury is again weighed, when perfectly cold, and from this the weight of the empty tube subtracted, the difference will give the quantity of the mercury produced. At the same time the volume of the oxygen may be measured and its weight determined from its volume and specific gravity.

If the experiment is carried out with care and with the neces-

sary precautions, it will be found that mercuric oxide always yields 92·6 per cent. of metallic mercury, and 7·4 per cent. of oxygen, or, reckoning the oxygen by volume, that 100 grammes of mercuric oxide give 92·6 grammes of mercury, and 5,170 c.c., or 5·15 litres of oxygen.

For the preparation of considerable quantities of pure oxygen, the best material is an artificial chemical compound very rich in this element—potassium chlorate. This salt, which is soluble in hot water, and crystallizes out on cooling in small plates, with a mother-of-pearl lustre, consists of the metal potassium and the gases chlorine and oxygen. It possesses the property of melting when heated, and of giving off all its oxygen with apparent boiling and frothing, the end product, a compound of its two other constituents—viz. potassium and chlorine—remaining behind. In this manner 100 grammes of potassium chlorate give 39 grammes of oxygen, or more than five times as much as that obtained by heating an equal weight of mercuric oxide.

This operation is best carried out in a retort of hard glass, as shown in fig. 3. The neck of the retort is connected by a moveable india-rubber tube with a glass tube which leads the gas into a gasometer, and expels the water as it enters.

In order to prevent the frothing over of the heated mass in the retort, the potassium chlorate may be mixed with an equal weight of dry pyrolusite (or oxide of copper) before putting it into the retort. Such a mixture does not melt when heated, and as the solid body mixed with it distributes the heat equally to the entire mass, the evolution of gas takes place without frothing, and much more quickly.[1]

If large quantities of oxygen are to be prepared, and a pound or more of the mixture of manganese peroxide and potassium chlorate heated at once, a cast-iron retort may be used, with a broad, flat edge (fig. 4). On this edge fits a cover with an enlargement at the top, and a tube for the escape of the gas. This cover is screwed fast, a lute of moist clay free from sand being used to make it air-tight. A large gas-burner placed underneath is sufficient to effect the decomposition of the potassium chlorate.

The chemical properties of a substance are shown by its behaviour to other bodies. Let us see how oxygen acts towards

[1] The manganese peroxide remains unchanged during the reaction; why it is that some substances cause the evolution of the gas at a lower temperature and others do not, has not yet been satisfactorily explained.—ED.

some of the better known chemical substances, and what phenomena may be observed at the same time.

Daily experience teaches us that a glowing chip of wood is soon extinguished in the air. But if it is dipped into a jar of oxygen it not only continues to glow, but at once bursts into flame. A piece of charcoal feebly glowing soon goes out in the air, but continues to burn with much greater heat and light when introduced into oxygen. Sulphur when heated in the air burns with a pale blue flame. But if a small piece is placed in an iron spoon, ignited, and then dipped into a jar containing oxygen, not only does the flame increase in size and brilliancy, but the sulphur also burns away more rapidly. We may readily convince ourselves of this by

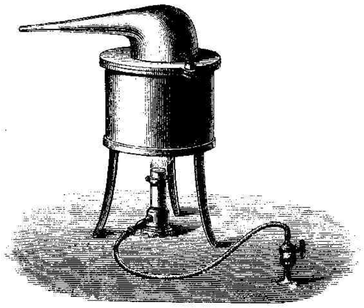

Fig. 4.

burning two pieces of sulphur of the same size, one in air and one in oxygen. Phosphorus, which catches fire so easily, and which even in common air burns brilliantly, if heated in an iron spoon and introduced into a large jar of oxygen, produces a light so intense that the eye cannot bear it, and so high a temperature that the glass vessel is often broken.

Iron, which melts and burns difficultly in the air, catches fire when previously heated and plunged into oxygen, burning with great brilliancy and a shower of sparks to form a new substance—a chemical compound of iron and oxygen. To perform this pretty experiment on a small scale it is best to employ a thin steel watch-spring. The spring is softened and bent into a spiral form, attached

at one end to a cork, and to the other end is fastened a small piece of tinder. The tinder is then set on fire and the whole plunged into a jar of oxygen. The tinder first burns with a bright flame, and then imparts its temperature of combustion to the iron, which is high enough to make the metal burn brightly with a shower of sparks (fig. 5). This phenomenon lasts as long as any unburnt oxygen remains, or until all the iron is consumed. The drops of the molten compound of iron and oxygen which fall down are so hot that they fuse into the bottom of the glass vessel, and often cause its destruction.

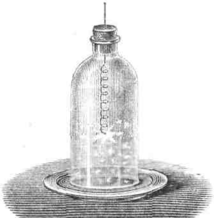

Fig. 5.

In the same manner as these substances, all bodies which burn in atmospheric air burn also in oxygen, and always with a much greater evolution of light and heat than we are accustomed to see in common air.

In all cases the products of the combustion are chemical compounds of the burnt body with oxygen. With charcoal and sulphur these products are not so perceptible as with iron, as they are colourless, transparent gases. But their presence may be easily made manifest to the eye. The gaseous product of the combustion of charcoal, carbonic acid, possesses the property of making a clear transparent aqueous solution of lime—lime-water—turbid, by the production of a new chemical compound of carbonic acid and lime, which is insoluble in water. If, therefore, we pour clear lime-water into the jar in which the charcoal has burnt, and bring it into close contact with the carbonic acid by shaking, the liquid becomes milky and afterwards deposits a white precipitate.

The gaseous product (sulphurous acid) of the combustion of sulphur may be recognized by its piercing acid odour, as well as by the reddening of the blue aqueous solution of litmus when this is poured into the jar in which the sulphur has burnt.

The product of the combustion of phosphorus—phosphoric acid—is really a solid body—a snow-white powder ; it dissolves, however, so easily in water that if the vessel in which the phosphorus was burnt contained a little moisture the compound at once disappears. The presence of this body, or generally that the com-

bustion of phosphorus produces a substance with strongly acid properties, may also be shown by the strong red colour which is at once imparted to blue litmus solution brought into contact with it.

It will be noticed that the chemical compounds produced by the combustion of sulphur and phosphorus are acid bodies; the same is also true for that body produced by the combustion of charcoal. At one time it was thought that all acids contained oxygen, whence its name, from ὀξύς, 'acid,' and γεννάω, 'I produce.' We now know that this is incorrect.

The apparatus which served originally for measuring volumes of gases, and called, therefore, gasometers, are now principally employed for the collection and preservation of gases. We have referred above to these instruments, which are provided with simple arrangements for allowing the gas to stream out under pressure of water as required, and so make it possible for the chemist to use the gas at any time.

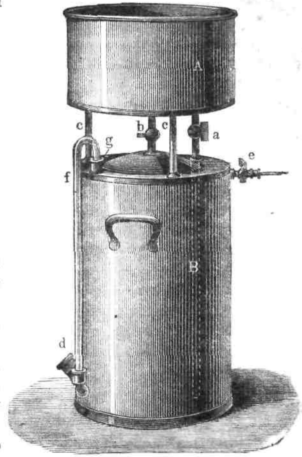

Fig. 6.

The construction of the gasometer is simple, and may be easily understood from the accompanying figure (fig. 6), and from fig. 3. It consists of two vessels of copper (or zinc), of which the lower one, B, is closed in all directions, while the upper and smaller one, A, is open at the top. Both communicate with two tubes, *a* and *b*, provided with stop-cocks, which, together with short thick rods *c*, *c*, serve to support the upper vessel. The tube, *b*, does not go further than just through the base of A and the top of B; the tube *a*, on the other hand, extends nearly to the bottom of the vessel B, and is open at the lower end. At the

side is another tube with the stop-cock *e*, which allows the gas contained in B to flow out when required.

The vessel B is first filled with water by pouring it into A, and opening the cocks, *a*, *b*, and *e*. The water flows in by the tube *a*, reaching nearly to the bottom of B, and displaces the air, which escapes by the tubes *b* and *e*, until the entire vessel is full. After all the stop-cocks have again been closed, the lower, wider tube *d* may be opened without water flowing out. The end of the tube, from the apparatus evolving the gas, is then inserted at *d*, and as the gas enters the vessel B it displaces the water which flows out by the side of the tube from *d*.

The extent to which the gasometer is filled with gas is shown by the height of the column of water in the glass tube *g*, *f*, which communicates with the interior of the vessel B, above and below, and in which the water is always as high as in the interior of the gasometer.

When the gasometer is filled as far as required, the tube is withdrawn, the screw at *d* replaced, and the stop-cock *a* opened. The gas enclosed in B is thus subjected to a pressure equal to the column of water from the surface of the water in B to that in A.

If the stop-cocks and joints of the gasometer are air-tight, the gas may be preserved in it for a long time. When a regular stream of gas is required, the tube *e* is connected with the apparatus by a piece of india-rubber tubing, and the stop-cock opened. If the gas is to be collected in a cylinder over water, the cylinder is filled with water, closed with a glass plate, and inverted in the water of the vessel A. The glass plate is then removed, and the stop-cock *b* opened, when the gas rises, the cock *a* being open, under the pressure of the difference between the column of water in and over the tube *a* and of that over the opening of *b* in the cylinder.

HYDROGEN.

Chemical Symbol: H.—*Atomic Weight*: 1.

Unlike oxygen, hydrogen does not occur in the free state in the earth's atmosphere, but recent physical investigations have shown that it is contained in the atmosphere of some of the heavenly

bodies, particularly in that of the sun. As a constituent of water, hydrogen is very widely distributed and in very large quantities; it is also contained in nearly all organic compounds, either as water or in some other form of combination. Hydrogen owes its name to the fact that it is an essential constituent of water (ὕδωρ, 'water,' and γεννάω, 'I produce').

Although hydrogen was prepared as early as the sixteenth century by Paracelsus, it was Cavendish who in 1781 first recognized it as an elementary body, and described its properties. Cavendish may therefore be rightly considered as the real discoverer of this element.

Hydrogen is a colourless gas without smell or taste, which cannot be respired, and which is even less soluble in water than oxygen. It was formerly included under the 'permanent gases,' but has now been condensed to a liquid; the pressure and cold required being even greater than in the case of oxygen (600 atmos. and $-140°$).

One of the most striking physical properties of hydrogen is its low specific gravity. Oxygen, as we have seen, is a little heavier than atmospheric air; hydrogen is so very much lighter that one volume of air weighs more than fourteen equal volumes of hydrogen. Its specific gravity is exactly 0·0692. One litre of hydrogen at 0° and under an air pressure of 760 mm. weighs 0·0895 gramme; while under similar conditions one litre of air weighs 1·293 gramme, and one litre of oxygen 1·429 gramme. Air is therefore 14·44 times as heavy as hydrogen, and oxygen 16 times as heavy. This property of hydrogen makes it better adapted than any other gas for filling balloons.

Water is principally employed for the preparation of hydrogen. The gas may be obtained, as we have previously seen (p. 6), by the decomposition of water into its two constituents by the electric current, and by collecting the gases in separate glass tubes, previously filled with water. Or, we may employ some body acting chemically, which, having a stronger affinity for oxygen than hydrogen has, unites with the former to produce a non-volatile chemical compound, and sets the latter free in the gaseous state.

To those elements which unite a very strong affinity for oxygen with a very weak attraction for hydrogen belong the metals potassium and sodium. If a small piece of sodium is thrown upon water, it swims on the surface with a hissing noise, evidently producing an evolution of gas. The piece gradually becomes smaller

until it completely vanishes. By this reaction the metal sets the hydrogen free from the water and unites with the oxygen; the oxygen compound of sodium so produced is then dissolved in the remaining water.

In order to collect the hydrogen evolved, and to recognize it as such, a small glass tube, closed at one end, may be filled with mercury and inverted in a trough containing the same substance. A little water is then introduced into the tube, and a small globule of sodium passed up. As soon as the sodium reaches the water in the tube a lively evolution of gas commences, the globule becomes smaller, and in a few seconds disappears. The gas which collects in the upper portion of the tube depresses the column of mercury and takes its place. If the tube is now closed with the thumb, re-inverted, and a burning chip brought near to the open end, the gas, which rapidly streams out on account of its lightness, catches fire and burns with a pale, scarcely luminous flame.

This method of obtaining hydrogen is very simple and instructive, but is not well adapted for the preparation of large quantities of the gas. We are acquainted with other metals that have a strong affinity for oxygen, and which can also decompose water, which, however, do not, like sodium, possess this property at the ordinary temperature, but only acquire it at a higher temperature, near a red-heat. To these belongs iron.

If an iron tube—*e.g.* an ordinary gas-tube—is filled with iron wire wound together, and then heated to redness in a furnace so that the ends project out for some distance, and if steam from boiling water in a retort is passed in at one end of the tube, the water is decomposed, its oxygen uniting with the iron to form a solid compound which incrusts the metal, while its hydrogen is set free from the other end of the tube. If a glass tube dipping under water is previously connected with this end of the iron tube, large quantities of hydrogen can be collected in inverted glass cylinders placed to receive it.

Iron acquires the property of decomposing water at the ordinary temperature, when a strong acid—*e.g.* sulphuric acid—is added to the water. Since, however, iron always contains carbon, and often other substances mixed with it, the hydrogen so obtained from this metal is always rendered impure from the admixture of other substances, particularly of gaseous hydro-carbons. It is therefore better to employ metallic zinc, which is easier to obtain in a fairly

pure state, and which, in this respect, behaves in just the same manner as iron.

As a vessel for generating the gas, a Woulff's bottle with two necks may be employed, which contains the zinc in the granulated state (fig. 7). In the one neck is a cork, fitting air-tight, which is pierced to receive a funnel-tube, passing to the bottom of the flask, and serving to pour in the acid. The other neck also contains a cork, carrying a glass tube just passing through it, by which the gas escapes and may be collected. For convenience in movement this glass tube is best divided into two parts connected together by an india-rubber tube. If now sulphuric acid strongly diluted with water is poured in by the funnel-tube, and so brought into contact

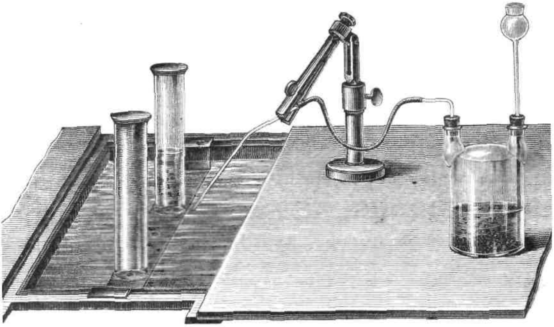

Fig. 7.

with the zinc, a copious evolution of hydrogen is at once produced with the development of heat. In the flask the salt called white vitriol (zinc sulphate) remains behind dissolved in the water.

Before commencing to collect the gas in the jars or in a gasometer, a certain quantity, not too small, must be allowed to escape into the air, until there is no doubt that all the air which was contained in the Woulff's bottle has been driven out. If a mixture of hydrogen and air is set on fire, the combustion would probably be accompanied by a powerful explosion, and the vessel shattered. (See Appendix.)

In its chemical behaviour, hydrogen is particularly distinguished

from oxygen by the fact that it is combustible; it takes fire when ignited in contact with air, and burns with a scarcely luminous flame.

The chemical properties of hydrogen generally are best seen in its behaviour to oxygen, in connection with which we have to consider four distinct questions:—

i. Under what conditions does the chemical combination of hydrogen and oxygen take place?

ii. What is the product of this union?

iii. With what phenomena is the chemical union of the two substances accompanied?

iv. What regularities do we observe in the process?

Oxygen and hydrogen gases, when mixed together in any proportion, remain chemically unchanged under ordinary circumstances for any length of time. Direct sunlight does not act upon the mixture, as it does on the mixture of other gases. But if such a mixture be raised to a certain temperature, for which the passage of an electric spark or contact with a burning chip of wood suffices chemical union at once follows, in this case with an explosion. In order that the hydrogen may unite with the oxygen, it must be raised up to or above a certain temperature, called its *temperature of ignition.*

The product of the combination of hydrogen and oxygen is under all conditions, water. Of this we may easily convince ourselves by a simple experiment.

Although it is dangerous to ignite a mixture of hydrogen and oxygen, a burning body may be safely brought near a jet of hydrogen gas issuing from a small opening—*e.g.* a glass tube—into the air. The gas then catches fire and burns with a pale flame If a tube, bent upwards at its point, is connected with a hydrogen apparatus or a gasometer containing hydrogen, the gas set on fire and the tube then dipped into a large glass flask containing dry oxygen, the flame of the hydrogen becomes smaller—and is at the same time tinged yellow—and the inner walls of the flask become covered with drops of dew. The longer the hydrogen burns in the oxygen the more does the flask become bedewed, and the greater is the quantity of water produced.

The same phenomenon is perceived when the flask is simply filled with atmospheric air, the oxygen of which then serves to convert the hydrogen into water.

If in this experiment oxygen is led into the flask at the same rate as it is consumed by the hydrogen, and if care is taken to keep down the high temperature produced by the combustion by cooling the outside of the flask, a considerable quantity of water may in time be produced from its constituents.

The chemical union of hydrogen and oxygen, whether continuous by burning the gas in air, or whether instantaneous by the explosion of the two gases previously mixed, is accompanied by a very large evolution of heat. In daily life the temperature of a flame is often judged by the light which it emits, and it is customary to consider the flame of a spirit-lamp less hot than that of a candle. The chemist knows that this measure of the temperature of different flames is wrong, and that the scarcely luminous flame of hydrogen burning in oxygen possesses one of the highest temperatures which we can produce by the processes of combustion. Platinum, which is so difficult to melt, and which remains unchanged in the strongest heat of our ordinary furnaces, may be easily fused in the oxy-hydrogen flame.

The explosive action produced by the ignition of a mixture of hydrogen and oxygen in the proper proportions and the danger attending these explosions make it necessary to be careful in experimenting with such a mixture of the two gases. If a large glass jar standing over water were filled two-thirds full with hydrogen and the other third with oxygen, the mouth closed with a glass plate, the jar inverted, and, at the moment when the plate was taken off, a burning taper applied, not only would the mixture burn with a loud explosion, but the glass cylinder would probably be broken.

It would be still more dangerous to ignite a gasometer full of the mixed gases by opening the upper stop-cock and applying a flame. Since the invisible particles of hydrogen and oxygen are most intimately mixed with one another, certainly much closer than we can bring the particles of two solid substances by rubbing them together, the ignition at one point of the gas would be immediately transmitted through the entire mass, and a loud explosion, with the destruction of the vessel, would be the result.

In order to exhibit this phenomenon in a harmless manner, the mixed gases must be enclosed in very thin membranes. A thin calf's bladder may be taken, but it is better and even less dangerous to explode the mixed gases in soap bubbles. The bubbles filled with the gases may be prepared in the following way.

About two volumes of hydrogen and one of oxygen are mixed in a glass bell-jar (*c*, fig. 8), standing over water, which is provided with a brass stop-cock. To this brass stop-cock is screwed on another stop-cock, to which is fastened a bladder softened in warm water and squeezed together to expel the air. If now both taps are opened and the bell-jar pressed down in the water, the mixed gases are forced up into the bladder. As soon as the bladder is filled the taps are again closed and the bladder unscrewed. On dipping then the end of a tube attached to the brass stop-cock of the bladder under a little soap and water in a saucer, opening the cock, and pressing the bladder gently, a large number of soap bubbles, filled with the mixed gases, may be obtained on the saucer. If then a burning taper is brought into contact with these soap bubbles, a violent explosion is produced, but without in the least damaging the saucer. The bubbles may even be exploded in the hollow of the hand without the least danger: no shock is experienced, but only a feeling of gentle warmth.

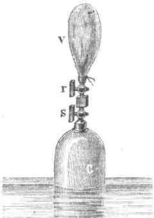

Fig. 8.

If a thin glass flask is filled with the explosive material, the mouth closed with a cork, and well wrapped in towels so that the mouth just projects, then on pointing the mouth towards a bare wall, withdrawing the cork and applying a flame, a smart explosion results, and the glass flask is burst into a thousand pieces, which remain in the towels.

A similar, though much less powerful action, is produced by the ignition of a mixture of two volumes of hydrogen and five volumes of common air.

In all cases the explosion is caused by the high temperature produced when a mixture of hydrogen and oxygen is burnt. The water vapour which is produced, and which is momentarily heated to redness, expands so largely and so suddenly that thin vessels cannot stand the pressure and are therefore burst. Immediately after this expansion follows the contraction and condensation of the hot water vapour to liquid water by the cooling which it suffers on coming into contact with the surrounding cold air. By this means a partially vacuous space is formed, and the rushing together of the surrounding air, together with the previous expansion, produces the

movement in the air which is perceived by the ear as the sound of the explosion.

If such expansions and contractions follow one another alternately, regularly, and quickly, they may set a column of air in vibration, and produce musical notes. This may be easily shown by lowering an open glass tube, of about a metre long, vertically over a flame of hydrogen gas, so that the flame continues to burn

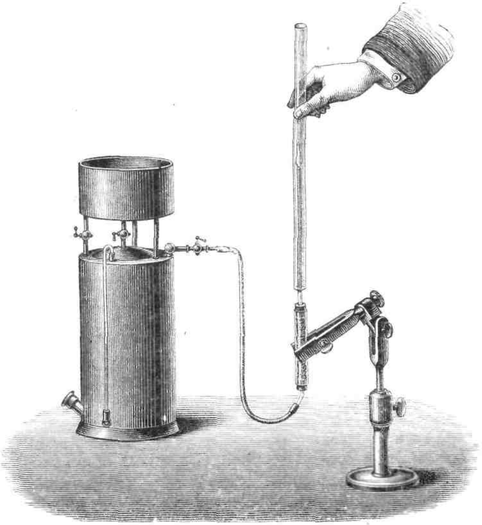

Fig. 10.

Fig. 9.

(fig. 9). The cold air rises rapidly in the tube, mixes with the hydrogen gas, and causes it to burn more energetically. And since the red-hot water vapour which is continually produced is as continually cooled by the ascending air, small vacuous spaces are formed, and the whole column of air is set into vibration. A musical note is therefore heard, the pitch of which depends partly

on the width and length of the tube, and partly on the position of the flame burning in it. In consequence of these vibrations the flame itself is altered in character and looks something like fig. 10.

Several practical applications are made of the high temperature produced by the combustion of a mixture of hydrogen and oxygen. Metals which do not melt at the highest temperature of our furnaces —*e.g.* platinum—may be easily fused by means of the oxy-hydrogen blowpipe. This blowpipe (fig. 11) is so arranged that the hydrogen and oxygen only mix at the moment when, and at the place where, they issue from the blowpipe. It consists of a copper tube, which opens into one of platinum, and into which hydrogen is led by the tap H. A second narrower tube of copper is placed inside the larger one, and also terminates in a platinum point. Oxygen is led into this tube by the tap O, and it can be raised or lowered at will.

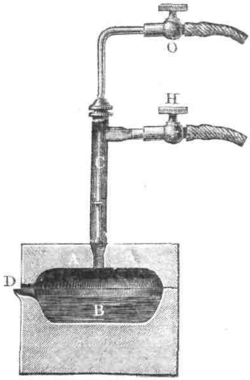

Fig. 11.

As crucible for the molten metal a block of quick-lime is used. This block is sawn through and hollowed out as shown in the figure. The lower piece B, which is provided with a spout D, receives the metal to be melted; the upper piece A is pierced at the top to receive the end of the blowpipe.

The highest temperature is obtained when the taps O and H are so placed that for one volume of oxygen two volumes of hydrogen are burnt, which may be easily seen from the nature of the flame after a little practice. The molten platinum is poured from the opening D.

Iron, copper, and other metals may also be easily melted in the same manner; but the fusion of those metals which become

oxidized in the presence of oxygen at a high temperature must be effected with an excess of hydrogen.

Lead, which belongs to the most easily fusible of the heavy metals, cannot be melted by a small flame, when in large plates, owing to its high conducting power for heat. In order to melt together air-tight the immense sheets of lead of which the chambers of the sulphuric acid works are constructed, the oxy-hydrogen blowpipe is successfully employed. Only the high temperature of this flame can suffice to melt together the edges of two thick plates of lead.

The high temperature of a burning mixture of hydrogen and oxygen is also used for the production of a brilliant light. The mixed gases when ignited produce a hardly luminous flame; but this flame can make solid infusible substances brought into it so hot that they give out the most intense light. Quicklime is particularly adapted for this purpose; it does not melt in the flame, but remains unchanged. The light which a piece of lime emits when it is brought into the oxy-hydrogen flame, with suitable arrangements, is so intense that it is used to illuminate large spaces at night, and is well adapted for signals—*e.g.* lighthouses. This source of light, which is also used for magic-lanterns and other purposes, is called the *lime-light*, or sometimes the *Drummond-light*, after Drummond, who first brought it into use.

The fourth of the questions previously asked (p. 20) remains unanswered: What regularities do we observe on the union of hydrogen and oxygen to form water?

We have already learnt (p. 6) that on the electrolysis of water with two platinum plates as electrodes exactly two volumes of hydrogen are set free for every one volume of oxygen. This leads to the conclusion that, on the *synthesis* of water, hydrogen and oxygen would unite in the same proportion. Experiment has, in fact, proved that if one volume of oxygen unites chemically with hydrogen, exactly two volumes of the latter gas are required, and that when an excess of either of the gases is employed, this excess remains behind unchanged. This regularity may be illustrated in the following manner.

An eudiometer of simple construction and sufficient for this experiment (fig. 12), is prepared from a glass tube of $1\frac{1}{2}$ centimetre internal diameter and 50 centimetres length. The upper end is closed, and two stout platinum wires are melted into it, of which

the ends are about 5 mm. from one another, and are connected together by a thin platinum wire. In order to *calibrate* this tube so that a number of equal volumes of gas may be marked outside, it is filled with water, inverted, and the air from a small measuring tube, about 5 mm. in diameter and 6 cm. in length, allowed to ascend into it. The eudiometer is next lowered in the cylinder (fig. 12) until the level of the water inside and outside the tube is the same, and then an india-rubber ring is slipped along the tube to mark the level of the water. After repeating this six or eight times, as many divisions of the tube are obtained, marked externally by the india-rubber rings, which need not be moved from their positions if the instrument is carefully handled.

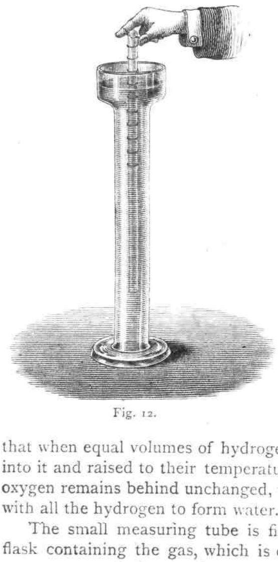

Fig. 12.

By means of this eudiometer it may be easily shown that when equal volumes of hydrogen and oxygen are introduced into it and raised to their temperature of ignition, one half of the oxygen remains behind unchanged, while the other half combines with all the hydrogen to form water.

The small measuring tube is filled with oxygen from a small flask containing the gas, which is closed with a cork and stands over water, and the gas is passed up into the eudiometer. The operation is repeated, and then two tubes full of hydrogen are passed up (fig. 13). In order to be quite sure that the mixture reaches to the fourth ring on the tube, the latter is transferred to the cylinder and lowered until the level of the water is the same inside and outside the tube.

The eudiometer is now closed with the thumb, and transferred to a small pan with water, for which an ordinary porcelain or glass mortar may be used, and firmly pressed with the hand on a thick piece of india-rubber at the bottom in order to prevent expulsion

of the gas on the explosion of the mixture (fig. 14). The ignition is brought about by connecting the two platinum wires at the end

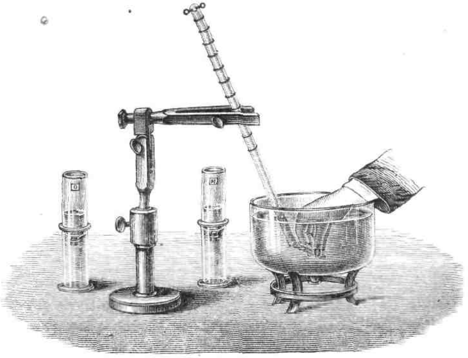

Fig. 13.

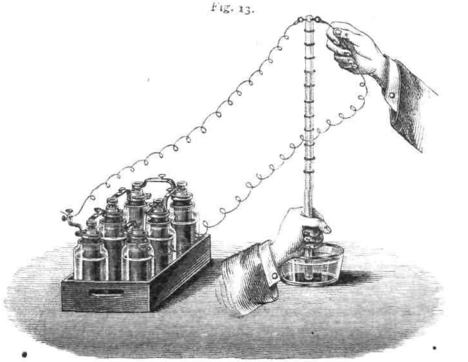

Fig. 14.

of the eudiometer with the wires from a battery of four or six Bunsen's cells. The electric current then heats the thin platinum

so strongly that it reaches the temperature of ignition of the mixed gases.[1] The combination is shown by a pale flash of light and a feeble, scarcely perceptible shaking of the tube.

That a condensation has taken place owing to the union of the two gases to form liquid water, or, in other words, that a diminution of the volume of the gases has been produced, only becomes visible when the eudiometer is slightly inclined and the india-rubber plate removed. The water then rises in the eudiometer, and when dipped in the cylinder reaches exactly to the first mark.

Of the four volumes of gases three have, therefore, apparently disappeared. That the small remaining quantity of gas is oxygen may be easily seen by closing the eudiometer with the thumb; inverting and plunging a glowing chip quickly into the gas, the chip at once catches fire.

If an alteration is made in the experiment by taking hydrogen in excess—for example, by taking three volumes of hydrogen and one volume of oxygen—of these four volumes one volume would also remain behind after the explosion, and would now be hydrogen. That the remaining gas is really hydrogen may be readily proved by its inflammability.

As will be easily understood, such experiments do not give exact nor even approximately exact results. The water over which the measurements are made always contains air which mixes with the other gases, and in apparatus constructed and managed in this way the influence of temperature and of pressure cannot be sufficiently taken into account. But the experiments suffice to show all they are intended to—viz. the proportion by volume in which hydrogen and oxygen unite to form water.

A further question which must also be mentioned here is, What space does the water gas occupy which is produced by the union of two volumes of hydrogen with one volume of oxygen, and in what proportion does the volume of the water gas stand to that of its components? Since water under the ordinary pressure of the air only becomes completely gaseous at 100°, the volume of the water gas must be measured at some temperature above 100°. Experiment teaches us that the volume of water gas, measured at

[1] Instead of connecting the two wires in the eudiometer with a thin one of platinum, we can leave the ends free without touching one another inside the tube. If we then connect the wires from the battery with an instrument called an induction coil and the wires from the coil with those of the eudiometer, sparks pass between these wires when the connections are completed.—ED.

a temperature of about 150°, which is produced from two volumes of hydrogen and one volume of oxygen also at the same temperature does not occupy three volumes as we might expect, but only two volumes. It follows, therefore, that when hydrogen and oxygen unite to form water gas a condensation of the volume takes place in the proportion of three to two.

Since we know the relative densities of hydrogen and oxygen, in what proportion by volume they combine with one another, and what condensation is produced on combination, we can easily find the relative density of water gas.

It has been proved that two volumes of hydrogen (weighing $2 \times 0{\cdot}0692$) combine with one volume of oxygen (weighing 1·1056) to form two volumes of water gas, whence—

2 vols. hydrogen weigh $2 \times 0{\cdot}0692$	. . .	= 0·1384
1 ,, oxygen	. . . .	= 1·1056
2 ,, water gas	. . . .	1·2440

and, therefore, one volume of water gas weighs $\frac{1{\cdot}2440}{2} = 0{\cdot}622$, a number agreeing almost exactly with the experimental results of its specific gravity.

COMBUSTION.

We have seen that a number of bodies—sulphur, charcoal phosphorus, iron, hydrogen, &c.—when heated to their temperature of ignition, burn in oxygen, and that the products are always compounds of the burnt bodies with oxygen.

It may be asked, Is oxygen the only gas in which combustible substances can burn? or Do other bodies also possess this property? Experiment has long answered this question.

Among other bodies which possess this property is the element chlorine—a greenish-yellow gas—which, together with the metal sodium, makes up common salt, and which may be easily obtained from this substance. If hydrogen is allowed to stream out of a small opening in a glass tube, is ignited in the air, and then plunged into a jar of chlorine, the gas goes on burning, and the yellow colour of the chlorine gradually disappears. The flame of

the hydrogen burning in chlorine is not yellowish as when it burns in oxygen, but of a greyish colour, and the product is not water but a gaseous compound of hydrogen and chlorine, possessing strongly acid properties, and called hydrochloric acid.

This one experiment proves, and it might be confirmed by hundreds of others, that other substances as well as oxygen can support the combustion of burning bodies.

The process of combustion in oxygen, which is by far the commonest, is distinguished from combustion in other gases, and is called *oxidation*. Sulphur, it is said, becomes *oxidized* or suffers oxidation when it burns in oxygen, or generally when it unites chemically with this substance.

Combustion, and particularly that of wood, belongs to the phenomena of nature which were earliest noticed by man. The knowledge of this process is as old as the observation that the heavenly bodies move—movements which were, however, recognized and their investigation attempted thousands of years before it was known that the earth moves round the sun. The process of combustion remained a secret to investigators even later. It was a century and a half after Galileo's words, 'e pur si muove,' before this process was first correctly explained by Lavoisier. The necessary prelude was the discovery of oxygen, which was closely followed by Lavoisier's theory of combustion.

The history of the theories of combustion teaches us, if anything can, how mere philosophizing on natural phenomena, without an experimental basis, is a vain and useless undertaking.

At the end of the seventeenth century, the celebrated German chemist Stahl put an end to the obscure and contradictory ideas of earlier centuries by his phlogiston theory. The known fact that wood when burnt on the hearth gradually disappears, and that something apparently leaves it with the flame, for only ashes remain behind, led Stahl to the hypothesis that wood and all combustible bodies must contain a volatile substance, which on their combustion is given off with the production of heat and often of light. This substance he called *phlogiston*, and the process of combustion *dephlogistication*. Sulphur, phosphorus, or charcoal, when burnt, were said to be dephlogisticated or deprived of their phlogiston, and the solid product of the combustion of iron was dephlogisticated iron.

When metallic iron was obtained by heating dephlogisticated iron with charcoal, it was said that the dephlogisticated iron

became phlogisticated, or provided with phlogiston. Iron would accordingly be a more complex substance than the product obtained on burning it.

This hypothesis—the *phlogiston theory*—imparted such a simple and satisfactory explanation to all the then known phenomena of combustion, that for more than half a century no one doubted its correctness. On the other hand, Stahl, as well as some of his contemporaries, had made observations which strongly contradicted the theory ; but no attention was then bestowed on them, and their importance was overlooked.

It had been long observed by various chemists, and was not discovered by Lavoisier, that many metals on dephlogistication—*i.e.* on burning—increased in weight, notwithstanding that they were supposed to lose phlogiston. That this loss of phlogiston ought not to produce an increase in weight, but a diminution, was however, considered of no importance.

Only after the discovery of oxygen by Priestley and by Scheele did Lavoisier prove, by numerous new determinations, that bodies on combustion simply combine with oxygen, and that the increase in weight is the same as that of the oxygen consumed.

This result, now so familiar to us, may be easily proved by a simple experiment. A small quantity of iron in the state of a fine powder is placed in a bulb-tube, and then accurately weighed. A stream of oxygen is now allowed to pass through the bulb-tube, and the iron is at the same time heated ; suddenly the latter begins to glow, and this heating effect is transmitted through the entire mass in consequence of the union of the iron and oxygen. If then the bulb-tube is again weighed, when perfectly cold, it will be found to have considerably increased in weight. The same method may also be employed in order to determine quantitatively how much oxygen is consumed by a known weight of iron.

It may be here remarked that although iron may increase in weight on combustion in oxygen, a piece of wood or a candle clearly diminishes in volume and weight when burnt. But in these cases appearances are deceptive. Chemists have determined not only that the substance of wax-candles increases in weight on burning, but also that the products of combustion weigh more than four times as much as the wax consumed. This is not ordinarily perceived, as these products of combustion are volatile and invisible to the eye.

That even a candle increases in weight on burning, or that the

products of combustion weigh more than the burnt wax, may easily be made visible by the apparatus shown in fig. 15.

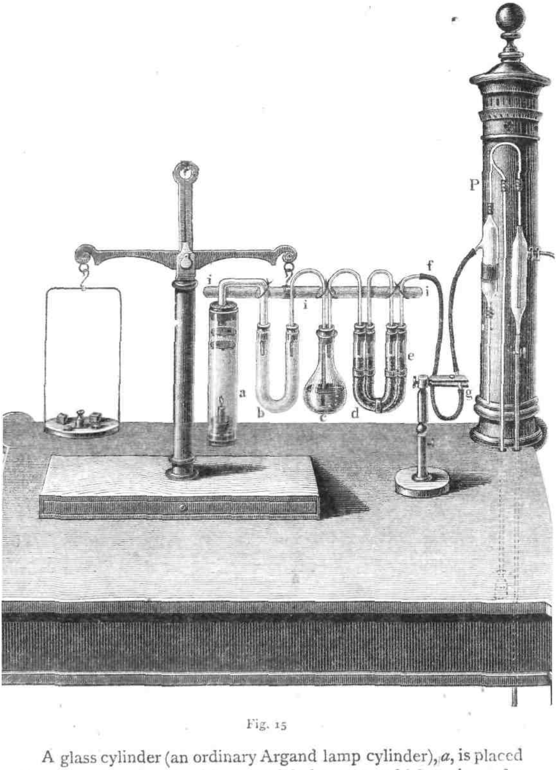

Fig. 15

A glass cylinder (an ordinary Argand lamp cylinder), *a*, is placed above a cork, pierced with several holes, upon which a piece of a

wax-candle, about two inches long, is fastened. The candle is surrounded with a small piece of tinfoil, which receives any molten wax running down.

The upper end of the cylinder is connected with a bent wide glass tube *b*, by means of an india-rubber stopper, and made to fit air-tight. In order to protect the stopper from the heated air rising from the flame, two perforated pieces of platinum foil are placed in the tube beneath it, care being taken that the perforations do not coincide with one another.

The vessels *b*, *c*, *d*, *e*, which communicate with the cylinder *a*, serve partly to retain the products of combustion of the wax, which consists of carbon, hydrogen, and a small quantity of oxygen, and partly to make these products visible to the eye. The tube *b* is empty, and receives a large portion of the water produced; the small flask *c* contains clear lime-water, which becomes milky when carbonic acid passes through it owing to the production of calcium carbonate; the tubes *d* and *e* are filled with pieces of caustic soda, which retain the remainder of the water and carbonic acid. A constant stream of air, which serves both to make the candle burn and to pass the products of combustion through the vessels *b*, *c*, *d*, *e*, is maintained by the Bunsen's pump P, which is in communication with these vessels by the india-rubber tubing supported at *g*.

The various portions of the apparatus are fastened to the glass-rod *i*, *i*, which is attached to one arm of an ordinary pair of scales, and is then exactly balanced by weights placed in the pan attached to the other arm. On opening the tap of the pump, no change takes place in the equilibrium. The candle is now carefully withdrawn, ignited, and again placed in the tube.

After a short time the inner surface of the tube *b* becomes covered with moisture, and at the same time the lime-water in *c* becomes turbid. And as the combustion proceeds, drops of water collect in the tube *b*, and the arm of the balance to which the apparatus is attached gradually sinks, until it rests on the foot of the instrument.

If the process is continued long enough to entirely consume the candle, a considerable weight must be placed in the pan of the balance in order to again restore equilibrium, which is sufficient proof that the substance of the candle, the wax, when burnt to carbonic acid and water, increases in weight.

We are so accustomed to see the burning of wood, oil, sulphur,

phosphorus, and other combustible bodies in the free atmosphere, that we are inclined at first to imagine that the burning bodies necessarily require a surrounding atmosphere rich in oxygen. This idea is also erroneous. If we drop a piece of phosphorus into a vessel of warm water, so that it melts, and then lead oxygen gas to it under the water in a slow stream, the phosphorus burns under the water, producing a considerable quantity of light and heat. The product is the same as when phosphorus burns in free air—viz. phosphoric acid.

For the conversion of phosphorus into phosphoric acid, the presence of free gaseous oxygen is not even a necessary condition. In nitric acid we are acquainted with a liquid chemical compound of nitrogen, rich in oxygen, which can be easily decomposed. If we heat a small piece of phosphorus in nitric acid, a portion of the oxygen of the latter body combines with the phosphorus without first assuming the gaseous state, and finally entirely oxidizes the phosphorus to phosphoric acid.

Metallic tin—*e.g.* tinfoil—which, when heated in the air or in oxygen, is converted into a white substance (stannic oxide, or putty powder), suffers the same change when acted on by nitric acid.

Charcoal may also be easily burnt by nitric acid to form carbonic acid. If a small piece of charcoal is made red-hot at one end, and dipped into a flask containing fuming nitric acid, so that the glowing point just touches the liquid, energetic combustion takes place, with a large evolution of light and heat.

In the same manner as free oxygen gas and the loosely united oxygen of nitric acid can oxidize combustible bodies, solid substances which contain their oxygen or a portion of it loosely combined may also be used for the same purpose. Powdered nitre—*i.e.* potassium nitrate—when sprinkled on a glowing coal, causes the latter to burn brilliantly to carbonic acid. Potassium chlorate acts in the same manner, and not only towards charcoal, but also towards other combustible bodies. If a small quantity of dry, powdered potassium chlorate is rubbed in a mortar with powdered sulphur (only very small quantities must be used), the heat produced by the rubbing is sufficient to cause a number of small explosions, depending upon the oxidation of the sulphur by a portion of the oxygen contained in the potassium chlorate; explosive compounds of chlorine containing less oxygen are also produced at the same time.

Ordinary combustions in oxygen are usually accompanied with

an evolution of light, and heat is always set free. In the case of some combustions, however, no light appears, and these are usually accompanied by less sensible heat. These processes of oxidation may be called slow combustion, in contradistinction to those producing light and sensible heat, called quick combustion. Phosphorus, which when heated in the air to its temperature of ignition burns quickly and brilliantly to phosphoric acid, also becomes oxidized at the ordinary temperature in the air, without any light being perceptible in the daytime. The product of oxidation in this case is an oxide containing less oxygen than phosphoric acid, and is called phosphorous acid. A piece of phosphorus, which when heated in the air undergoes quick oxidation and is converted into phosphoric acid in a few minutes, requires as many months, or even longer, to be completely converted into phosphorous acid by slow combustion.

The continuous oxidation produced in the human body by inspired oxygen belongs to those processes of slow combustion which are unaccompanied by any evolution of light. The oxygen brought into the lungs by inspiration is taken up by the arterial blood, and is so distributed to various parts of the body. It then oxidizes the various tissues of the body with which the blood comes in contact, as well as portions of the blood itself, being converted into water and carbonic acid. The latter substance is chiefly taken up by the venous blood and discharged from the lungs in the expired air. That the expired air is rich in carbonic acid may be easily shown by blowing through lime-water with a piece of glass tubing; the clear liquid becomes milky, and deposits a white sediment of calcium carbonate.

We know that when hydrogen is allowed to stream from a jet into the air, and a burning body brought near, it catches fire and burns; but we might in vain attempt to ignite oxygen under the same conditions. Suppose, however, the earth were surrounded with an atmosphere of hydrogen, instead of with one of common air, and that its inhabitants required hydrogen gas just as we do oxygen, how would oxygen behave if a jet of it were heated in this atmosphere of hydrogen? Would it then also burn with a flame in the same manner as hydrogen in oxygen?

Experiment has answered this question in the affirmative. It may be easily shown that oxygen burns in hydrogen, just as hydrogen in oxygen. If oxygen is allowed to flow slowly from a gas-

ometer out of a glass tube bent upwards, and a large inverted jar of hydrogen which has been previously ignited is placed over the jet, it will be seen that the oxygen catches fire and burns in the atmosphere of hydrogen with a pale flame, until all the latter gas is consumed.

From this it is clear that the distinction between combustible bodies and supporters of combustion is not strictly scientific, and is as inexact as when we speak of the rising and setting of the sun. We must consider the process of combustion in the wide meaning of the word as the chemical union of heterogenous bodies, and in the narrower meaning as an oxidation process, or the union of a substance with oxygen.

The oxygen may be more or less easily again separated from the oxidized bodies. It is only necessary to heat the red oxide of mercury, oxide of silver, or the oxides of the other noble metals, in order to drive out the oxygen and to obtain the metal again. If we pass hydrogen over the product of combustion of copper (black oxide of copper), and apply heat, the gas unites with the oxygen to form water, and metallic copper remains behind as a red powder. The powerful affinity which carbon has for oxygen at a red heat makes it well adapted for abstracting the oxygen from the oxides of those substances (*e.g.* phosphorus and iron), which possess strong affinities for oxygen. By means of glowing charcoal we can reduce phosphoric acid to phosphorus, and oxide of iron—*e.g.* the iron-ores employed in blast furnaces—to metallic iron.

By the processes of reduction we produce exactly the opposite effect to those of combustion, or more correctly of oxidation generally. We understand by *reduction* not only the production of the elements from their oxygen compounds, but also their separation from compounds with other substances. We reduce chloride of silver by separating the silver in some suitable manner from chlorine; we reduce mercury from cinnabar (mercuric sulphide) by the removal of the sulphur, &c.

Other reactions are also called processes of reduction, by which compounds of oxygen, sulphur, chlorine, &c., are converted into other compounds containing less of these last-named elements. We *reduce* the salts of ferric oxide to those of ferrous oxide, which contain less oxygen, cupric chloride to cuprous chloride, containing less chlorine, sulphuric acid to sulphurous acid.

In the same manner oxidation means not only the combination

of a substance with oxygen, but also the addition of more oxygen, sulphur, chlorine, &c., to compounds already containing these elements. We *oxidize* the salts of ferrous oxide to those of ferric oxide, cuprous chloride to cupric chloride, sulphurous acid to sulphuric acid, &c.

THE LAWS OF CHEMICAL COMBINATION.

We have seen that the union of hydrogen and oxygen to form water always takes place according to a definite proportion. Exactly two volumes of hydrogen always combine with exactly one volume of oxygen. Now since we know the specific gravity of the two gases, or that one volume of oxygen (sp. gr. = 1·106) weighs 16 times as much as one volume of hydrogen (sp. gr. = 0·069), it follows that the quantity of oxygen (one volume) which unites with two volumes of hydrogen weighs 8 times as much as the hydrogen. From this, the percentage composition of water by weight may be easily calculated :

2 vols. hydrogen	$= 2 \times 0·069 = 0·138$
1 „ oxygen	$= 1·106$
	1·244

If, then, x is the weight of hydrogen and y the weight of oxygen contained in 100 parts by weight of water, we get the following simple proportions :

$$1·244 : 0·138 :: 100 : x,$$
$$1·244 : 1·106 :: 100 : y,$$

which give $x = 11·11$ and $y = 88·89$, and hence 100 parts of water contain :

Hydrogen	= 11·11 parts.
Oxygen	= 88·89 „
Water	= 100·00 „

This percentage composition of water, calculated from the proportions by volume in which hydrogen and oxygen unite with one another and from the specific gravities of the two gases, agrees exactly with innumerable analyses and syntheses of water which

have been made from time to time.[1] It has been further proved that pure water, whatever may be its source, whether obtained from ice, snow, or water vapour, or whether prepared artificially from its constituents, has always the same composition.

A chemical compound containing oxygen and hydrogen, like water, but in some other proportion, is not water. We are acquainted with such a compound, called hydrogen peroxide, to which we shall refer later on. This body contains only 5·9 per cent. of hydrogen, and 94·1 per cent. of oxygen.

The composition of all the more accurately known chemical compounds has, like that of water, been carefully determined, and we know not only of what elements they consist, but also in what proportions they contain these elements.

From these results of analytical chemistry two laws of extreme importance in discussing the regularities in the composition of chemical compounds have been deduced :—

i. *On the chemical union of two substances their original weight remains unchanged.*

ii. *Every chemical compound contains the simple substances of which it is composed in one, and only one, proportion by weight.*

From this, however, it does not follow that two substances which contain the same simple substances in the same proportions are therefore identical. Numerous *isomeric* compounds exist, which, although they have the same elementary and percentage composition, possess different properties, and are quite different bodies.[2]

[1] One of the simplest methods for determining the composition of water by weight depends upon the fact that red-hot copper oxide is reduced in a stream of hydrogen to metallic copper, while its oxygen unites with the hydrogen to form water. If we collect this water by some compound which will absorb it (*e.g.* calcium chloride) and weigh the tube containing this substance before and after the experiment, we know the weight of water which has been formed. And if we also weigh the copper oxide before and after the experiment we find the weight of oxygen which has combined with the hydrogen to produce the known weight of water. It is then always found that 100 parts by weight of water contain exactly 88·89 parts by weight of oxygen, the remaining 11·11 parts being hydrogen.—ED.

[2] Isomeric compounds, or those possessing the same percentage composition, may be divided into two classes—viz. those which have the same molecular weight, but in which the atoms are differently arranged—*e.g.* propionic acid $\left\{\begin{matrix} C_2H_5 \\ CO \cdot OH \end{matrix}\right.$, and methyl acetate $\left\{\begin{matrix} CH_3 \\ CO \cdot OCH_3 \end{matrix}\right.$, called *metameric* compounds ; and those of which the molecular weight of the one is some multiple

		Water		Copper Oxide		Lead Oxide		Thallium Oxide	
I.	a	Oxygen .	88·9	Oxygen .	20·15	Oxygen .	7·175	Oxygen .	3·774
		Hydrogen	11·1	Copper .	79·85	Lead .	92·825	Thallium	96·226
			100·0		100·00		100·000		100·000
	b	Oxygen .	100	Oxygen .	100	Oxygen .	100	Oxygen .	100
		Hydrogen	12·5	Copper .	396·25	Lead .	1293·7	Thallium	2550·0
	c	Oxygen .	8	Oxygen .	8	Oxygen .	8	Oxygen .	8
		Hydrogen	1	Copper .	31·7	Lead .	103·5	Thallium	204
		Sulphuretted Hydrogen		**Copper Sulphide**		**Lead Sulphide**		**Thallium Sulphide**	
II.	a	Sulphur.	94·118	Sulphur .	33·543	Sulphur .	13·39	Sulphur .	7·27
		Hydrogen	5·882	Copper .	66·457	Lead .	86·61	Thallium	92·73
			100·000		100·000		100·00		100·00
	b	Sulphur.	100	Sulphur .	100	Sulphur .	100	Sulphur .	100
		Hydrogen	6·25	Copper .	198·12	Lead .	646·8	Thallium	1275
	c	Sulphur.	16	Sulphur .	16	Sulphur .	16	Sulphur .	16
		Hydrogen	1	Copper .	31·7	Lead .	103·5	Thallium	204
		Hydrochloric Acid		**Copper Chloride**		**Lead Chloride**		**Thallium Chloride**	
III.	a	Chlorine	97·26	Chlorine .	52·827	Chlorine.	25·54	Chlorine.	14·82
		Hydrogen	2·74	Copper .	47·173	Lead .	74·46	Thallium	85·18
			100·00		100·000		100·00		100·00
	b	Chlorine	100	Chlorine .	100	Chlorine.	100	Chlorine.	100
		Hydrogen	2·817	Copper .	89·3	Lead .	291·56	Thallium	574·66
	c	Chlorine	35·5	Chlorine .	35·5	Chlorine.	35·5	Chlorine.	35·5
		Hydrogen	1	Copper .	31·7	Lead .	103·5	Thallium	204

The knowledge of the composition of the thousands of chemical compounds at present known to chemists would have been of little service to us had we been compelled to rest satisfied with this alone. But this knowledge serves as a foundation for determining and establishing the laws in which the elements combine with one another, and compounds with compounds.

The lines I.*a*, II.*a*, III.*a*, in the accompanying table give the percentage composition of compounds of hydrogen, copper, lead, and thallium with oxygen, sulphur, and chlorine respectively. The merest glance at these numbers shows that they are very different from one another, and that no apparent regularity exists between them. The only regularity which occurs in these three lines is that copper unites with less oxygen, sulphur, or chlorine than hydrogen, lead with still less, and thallium least of all. This is made more manifest in the lines I.*b*, II.*b*, III.*b*, in which are stated the relative weights of hydrogen, copper, lead, and thallium, which unite with 100 parts of oxygen, sulphur, and chlorine respectively. If we divide the numbers in line I.*b* by the smallest (12·5) the proportion becomes :—1 : 31·7 : 103·5 : 204, this is the ratio in which the four elements unite with 8 parts of oxygen (line I.*c*). When the numbers in line II.*b* are divided by 6·25, the proportion is the same as in line I.*b*; in like manner, this is the ratio in which the four elements unite with 16 parts of sulphur. The numbers in line III.*b*, when treated in the same manner, yield the same proportion; and this also is the ratio in which the four elements combine with 35·5 parts of chlorine.

Here, then, we at once perceive definite regularities which may be formulated in the following statement :—

The same proportional weights of hydrogen, copper, lead, and thallium always unite with one definite weight of oxygen, sulphur, or chlorine.

These elements do not, however, occupy any exceptional position, and all that has been said for their combining proportions holds also for all the others. We thus obtain the following general law :—

The proportion in which two bodies (A and B) combine with a third (C) is also the proportion in which they unite with all other bodies as well as with one another.

of that of the others—*e.g.* ethylene (C_2H_4) and propylene (C_3H_6), called *polymeric* compounds. Examples of these compounds are more common in organic than in inorganic chemistry.—ED.

Thus, from the accompanying table, we see that the weight of chlorine (35·5 parts) which unites chemically with 1 part of hydrogen is the same as that which unites with 31·7 parts of copper, 103·5 parts of lead, or 204 parts of thallium. And, again, that the same relative quantities of hydrogen, copper, &c., which unite with 35·5 parts of chlorine combine also with 16 parts of sulphur or with 8 parts of oxygen.

We have thus obtained the following numbers for these elements, which represent the relative weights in which they combine with one another and with other elements :—

Hydrogen	1·0
Oxygen	8·0
Sulphur	16·0
Chlorine	35·5
Copper	31·7
Lead	103·5
Thallium	204·0

Again, suppose we wish to discover in what proportions chlorine and oxygen unite with one another, it is sufficient to know the proportions in which they combine with a third body. We see from the preceding table that 103·5 parts of lead combine with 8 parts of oxygen or 35·5 parts of chlorine. The proportion 8 of oxygen to 35·5 of chlorine is therefore that in which these two elements unite with one another. Hypochlorous anhydride contains exactly 8 parts of oxygen united with 35·5 parts of chlorine.

In this manner the number representing the quantity of any other element which combines with 1 part of hydrogen, 8 parts of oxygen, 35·5 parts of chlorine, &c., may be easily obtained.

If we wish to find this number for the metal sodium, and know that the percentage composition of its compound with chlorine (common salt) is :

Sodium	39·32
Chlorine	60·68
	100 00

we need then only calculate the quantity of sodium which would combine with 35·5 parts of chlorine. This we find to be 23 from the proportion : $60·68 : 39·32 :: 35·5 : n$, and this number, therefore, expresses the weight of sodium which combines with 1 part of hydrogen, 8 parts of oxygen, 16 of sulphur, &c.

The relative weights in which bodies combine with one another,

and in which they displace one another from their compounds, are called their *equivalent weights*: 31·7 parts of copper, or 103·5 parts of lead always combine with 8 parts of oxygen, 16 of sulphur, or 35·5 of chlorine. If in a compound of 35·5 parts of chlorine and 103·5 parts of lead, the lead were displaced by some other substance—*e.g.* copper or hydrogen—the quantity of this substance required would not be the same as the lead displaced, but 31·7 parts of copper, or 1 part of hydrogen, would be necessary. In these compounds 1 part of hydrogen has the same effect as 31·7 parts of copper or 103·5 parts of lead, and these elements, therefore, displace one another in their compounds not in equal but in equivalent weights.

In order to displace 35·5 parts of chlorine from its compound with 1 part of hydrogen or with 204 parts of thallium by iodine, 127 parts of the latter body are required. On the other hand, to displace the 204 parts of thallium by hydrogen, only 1 part is necessary. Finally, if in the compound called copper sulphide, consisting of 16 parts of sulphur united with 31·7 parts of copper, silver be substituted for copper, it is found that 16 parts of sulphur unite with 108 parts of the former metal.

THE LAW OF MULTIPLE PROPORTIONS.

The number of chemical compounds would be very limited if the elements could only combine with one another in one single proportion. Experiment has, however, shown that most of the elements can unite with other elements in more than one proportion, many even in five different proportions, thus producing compounds which are usually very different from one another.

In such cases, however, the relative quantities of the two elements combining together are always some multiple of their equivalent weight by small whole numbers. As an example of this may be instanced the five compounds of nitrogen and oxygen, nitrous oxide, nitric oxide, nitrous anhydride, nitric peroxide, and nitric anhydride.

These compounds contain their constituents in the following proportions by weight.

	Nitrogen, parts	Oxygen, parts	Parts
Nitrous oxide . . .	14	8	
Nitric oxide	14	16	$=8\times2$
Nitrous anhydride . .	14	24	$=8\times3$
Nitric peroxide . . .	14	32	$=8\times4$
Nitric anhydride . .	14	40	$=8\times5$

From which it is at once seen that the quantities of oxygen united with one equivalent of nitrogen (14 parts) are multiples of its equivalent weight by the simple integers 1 : 2 : 3 : 4 : 5.

In the same manner one and the same quantity of iron unites with two different quantities of chlorine which are to one another in the proportion 2 : 3.

These and innumerable other results form the experimental basis of the *Law of Multiple Proportions*, which may be expressed as follows:—

The elements unite either in their equivalent weights or in simple multiples of their equivalent weights.

The law likewise holds for compounds as well as elements; when the former combine to form more complex compounds they do so either in their equivalents or in simple multiples of their equivalents. The statement of this law is due to Dalton: it is only about seventy years old. Dalton first published his theory in detail in the year 1808, at a time when exact chemical investigation was largely carried on in England, France, and Sweden, but when the leading chemists in Germany, following an erroneous path in natural philosophy without any real foundation of fact, long wasted their powers in worthless speculation.

The theories of Dalton and his conclusions derived from the law of multiple proportions were, however, more permanent and fruitful.

THE LAW OF VOLUMES.[1]

Not only is there a simple relation between the *weights* in which the elements combine together chemically, but for elements in the gaseous state there is also a simple relation between the

[1] The Editor is responsible for this statement of Gay-Lussac's law.

volumes of the constituents and of the compound, if gaseous, which is produced.

It will be remembered that when hydrogen gas and oxygen gas unite with one another chemically, they always do so in the proportion of two volumes of the former to one volume of the latter, and the volume of the water vapour produced (above 100°) is always two volumes. Further, one volume of hydrogen gas always unites with exactly one volume of chlorine gas, producing exactly two volumes of the gaseous compound called hydrochloric acid.

These may serve as examples of a general important law—the law of volumes—which may be formulated as follows :—

The volumes of two gases uniting chemically with one another are always in some simple proportion, and the volume of the compound produced, when gaseous, is also always in some simple proportion to those of its constituents. This law also holds for compound as well as for elementary gases. We owe its discovery to the celebrated French chemist Gay-Lussac, after whom it is often called.

THE ATOMIC THEORY AND CHEMICAL VALENCY OR ATOMICITY.

The stability with which two elements remain combined after their chemical union, the impossibility to again recognize in water, for example, any property of either of its components, and again to break up water by any mechanical means into hydrogen and oxygen, led to the idea that on the chemical combination of two bodies a penetration of matter and a similar coalescence occurred as that when a mixture of copper and zinc are melted together to form brass. In such alloys neither of the constituents can be distinguished or separated by mechanical means. It is impossible, even with the most powerful microscope, to perceive the copper and zinc in brass, or the gold in gold amalgam. Still, these alloys are not generally considered as chemical compounds, because the metals of which they are composed generally unite in almost any proportion, while the combination of bodies to form real chemical compounds always takes place in certain definite proportions.

If we melt together copper and zinc in those proportions by weight in which they both unite with oxygen, sulphur, chlorine, &c.

—*i.e.* in their equivalent weights, an alloy is produced which might be considered as a chemical compound; but such an alloy is also produced when we employ a little more or a little less copper or zinc than exactly corresponds to their equivalent weights. In no case does either copper or zinc remain behind unchanged, so that we can separate it from the compound.

But it is otherwise with real chemical compounds. As the metals may be fused together in any proportion, so may hydrogen and oxygen be intimately mixed in all proportions. But if we transform this mechanical mixture of the two gases into their chemical compound—viz. water, we know that the smallest quantity of hydrogen or oxygen present in the mixture above the equivalent proportion remains behind uncombined and unchanged.

If the chemical union of two substances depended upon an intimate coalescence and penetration of the two bodies, it would be difficult to understand why combination only occurs in certain definite proportions by weight, and it would be incomprehensible that, when it does occur in different proportions, this only happens *per saltum*, in simple multiple proportions.

Dalton's *atomic theory* affords a simple and satisfactory explanation of these results.

We believe, as Dalton did, that the substances which compose chemical compounds are not capable of indefinite division, but that they consist of particles, which cannot be further divided, either by physical or by chemical means. These particles are therefore called *atoms*. We imagine that chemical combination is produced by the attraction and juxtaposition of the atoms. The more firmly the atoms are united together, the stronger must be the force by which the combination is produced and maintained. This chemical force of attraction is quite different from any other physical force. It differs, for example, from the force of gravity, which acts through great distances, by which the earth is attracted to the sun, and a falling stone to the earth; it differs also from the forces of cohesion and adhesion. Chemical attraction never acts at a distance, like gravity, but requires immediate contact of the two bodies, just as the passage of an electric current requires the direct contact of the conducting bodies. Chemical attraction, as we have seen (p. 5), differs also from cohesion, by producing a material change in the bodies upon which it acts.

The chemical force which resides in the atoms, called *chemical affinity* or *attraction*, is evidently related to the force of electricity.

Many chemical processes are produced by electricity—combinations as well as decompositions. In the electrolysis of water, the hydrogen atoms are set free at the negative pole, and the oxygen atoms at the positive pole. And since bodies charged with opposite kinds of electricity attract one another, the conclusion might be drawn that the hydrogen which passes to the negative pole is charged with positive electricity and the oxygen with negative.

In the same manner, on the electrolysis of metallic salts, the metals are liberated at the negative pole, and the acids or similar constituents at the positive pole.

From these and other similar results, it was thought that the atoms were charged in different degrees with positive or negative electricity, and that the combination of two heterogeneous atoms was caused by the attraction of the different electricities: this was the fundamental idea in the *electro-chemical theory*.

But this theory leaves so many phenomena unexplained, and even contradicts many chemical reactions, that we do not at present employ it, although the existence of near relations between chemical and electrical forces cannot be denied. The fact which particularly contradicts the theory is, that the atoms of one and the same element, which were supposed by the theory to be charged with the same kind of electricity, attract one another and generally form very stable compounds.

We content ourselves with the hypothesis that a force producing chemical phenomena resides in the elementary atoms, and that the atoms of the elements, according to their nature, offer one or more points of attraction to other atoms.

When the atoms of heterogeneous elements attract one another by the forces present in them, and form a chemical compound, the number of the atoms of the one element which can be attracted by one atom of the other element is always limited, and, as we may imagine, depends upon the number of points of attraction which the atoms possess. This number is different with different elements.

We know that when hydrogen and chlorine unite with one another chemically they always do so in *one* definite proportion. From this and other results we conclude that the atom of hydrogen only offers *one* point of attraction to that of chlorine and to those of other elements.

The result that when hydrogen unites with oxygen to form water twice as much of the former gas is required as when it unites with chlorine leads to the conclusion that the atom of oxygen

possesses *two* points of attraction with which it secures the two atoms of hydrogen.

When carbon unites with hydrogen to form marsh gas and with oxygen to form carbonic acid, the carbon atom does not fix the same number of atoms of the two substances. The atom of carbon, as proved from the composition of innumerable compounds, possesses *four* points of attraction for the atoms of other elements, and therefore requires four atoms of hydrogen for saturation and only two of oxygen, which offer, not one, but two points of attraction to other atoms.

Two atoms of oxygen thus play the same part, in combination with one atom of carbon and with all other elements, as four atoms of hydrogen; or, what is the same thing, one atom of oxygen has the same value or valency as two atoms of hydrogen.

Those elements of which the atoms, like those of hydrogen, only possess one point of attraction are called *monads* (monovalent or monatomic), those with two points of attraction *diads* (divalent or diatomic), those with three *triads* (trivalent or triatomic), those with four *tetrads* (tetravalent or tetratomic), &c. No elementary atom appears to possess more than seven or eight points of attraction, and, as we have remarked, the number of atoms of an element which can be fixed by one elementary atom is, therefore, limited.

Although there are some organic compounds which contain several dozen atoms united with one another, we know how to resolve these apparently complicated proportions into others more simple, resembling the inorganic compounds.

The power of the elements to fix a certain number of the atoms of other elements is called their *atomicity* or *valency*, and we say that the atomicity of hydrogen is *one*, that of oxygen *two*, and that of carbon *two* or *four*. Every element possesses a definite greatest atomicity, or, in other words, a certain maximum number of points of attraction of its atom for other atoms. But the atoms of those elements possessing higher atomicity do not always exert their full power. Sulphur, of which the maximum atomicity is six, and which occurs as a hexad element in sulphuric acid, plays the part of a tetrad in sulphurous acid, and of a diad in sulphuretted hydrogen.

We imagine that when all the points of attraction of an atom are not active they are in a state of rest, or that they are latent, until aroused by some new chemical action. Two of the points of

attraction of nitrogen, the atom of which is pentad in ammonium chloride, are latent in ammonia, in which this element plays the part of a triad. The addition of hydrochloric acid, or indeed of any acid, to the ammonia suffices to awaken these two latent points of attraction and to convert the compound of triad nitrogen into one of the pentad element.

In other cases the action of heat or light is also necessary to make the latent points of attraction active. The four points of attraction of the atom of carbon, of which in the compound with oxygen called carbonic oxide only two are saturated, obtain their full value by combination with oxygen to form carbonic acid at a high temperature, or by combination with chlorine, producing phosgene gas under the influence of direct sunlight.

We say that sulphur plays the part of a diad element, or, more briefly, that it is a diad in sulphuretted hydrogen, that it is a tetrad in sulphurous acid, and a hexad in sulphuric acid; and we speak of diad carbon in carbonic oxide, of triad nitrogen in ammonia without touching the question of what may be the *highest* atomicity of these elements. We simply pay regard to the results of experiment, according to which the elements unite with one another in certain multiple proportions.

The chemical compounds which are produced by the union of the atoms are mechanically indivisible, but can be decomposed into their constituents by chemical forces. The smallest quantity of a chemical compound which can exist in the free state is called a *molecule.* By a molecule of water we mean the compound of two atoms of hydrogen with one atom of oxygen; by a molecule of carbonic acid, the compound of one atom of carbon with two atoms of oxygen.

The molecules of water, carbonic acid, iron sulphide, &c., are just as little perceptible or visible as the atoms. What we call water is an agglomeration of water molecules, and in the same manner the gaseous or solid carbonic acid collected in a vessel consists of a large number of carbonic acid molecules.

The question may here be asked, Are the elements as we know them—*e.g.* ordinary hydrogen gas or solid sulphur—agglomerates of their respective atoms? Not long ago this was thought so; we now know that the atoms of the elements can combine not only with the atoms of other elements, but also with themselves.

When atoms of hydrogen are set free from a chemical com-

pound, and when no other substance is presented to them for which they possess a stronger affinity, they unite with one another to form molecules of hydrogen. By the chemical union of two atoms of hydrogen a molecule is produced, and in the same manner a molecule of oxygen consists of two atoms of this element, a molecule of nitrogen of two atoms, &c.[1] In the molecules produced by the union of the atoms of the same element, the homogeneous atoms are not bound together with less, but often indeed with greater, affinity than in the compounds of heterogeneous elements. For example, the molecule of nitrogen is a much more stable compound of the two atoms of the element than the compounds of nitrogen with oxygen, or with hydrogen or chlorine.

Molecules of the same substance never exercise chemical action upon one another. Chemical combination or decomposition always occurs between the constituents of the molecules of different bodies. Two molecules of hydrogen act upon one another as little as do two molecules of chlorine, but if hydrogen and chlorine are mixed, and exposed to the action of light or heat, a decomposition of the molecules of both elements ensues, with the mutual exchange of the atoms of each. Two molecules of hydrochloric acid are produced from one molecule of hydrogen and one of chlorine. And although in this case, as in all others, it appears to be the molecules which act upon one another, it is in reality the atoms which unite with one another, and which are separated from molecular combination at the moment when the reaction commences.

We know from experiment that the elements at the moment of their liberation from a compound act more energetically upon substances with which they come in contact than in their ordinary (molecular) condition. Hydrogen and sulphurous acid in the dry state or in the presence of water have no action at all upon one

[1] Different molecules may exist of those elements which have a higher atomicity. It is possible that, besides the molecule of nitrogen, which perhaps consists of the two atoms of triad nitrogen united by their three points of attraction, a second kind of nitrogen molecule may exist in which the two atoms are united together by five points of attraction. Up to the present we only know one kind of nitrogen ; but phosphorus, sulphur, charcoal, and other elements exist in different forms or modifications. It is possible that the ordinary phosphorus, which is so easily ignited, owes its difference from the red amorphous phosphorus, a body endued with much less chemical affinity, to some such cause.

another, but if we add sulphurous acid to a mixture of zinc and sulphuric acid, which evolves hydrogen, the hydrogen at the moment when it is set free (in the *nascent state*) exercises a chemical action upon the sulphurous acid: it separates the molecules of this compound, uniting with the sulphur to form sulphuretted hydrogen, and with the oxygen to form water.

We explain this and all similar phenomena by the hypothesis that in the *nascent state* the atoms, not the molecules, exert the chemical action, and that the atoms, with their entire force, naturally produce chemical changes which the elements in their molecular state—after the elementary atoms have united together—cannot effect.

AVOGADRO'S LAW.[1]

We have here to refer to a very remarkable law concerning the number of molecules contained in different gaseous substances. This law, which is proved from the physical properties of gases may be thus stated :—

Equal volumes of all gases, both elementary and compound, when under the same physical conditions—i.e. at the same temperature and under the same pressure—contain an equal number of molecules.

It follows from this that molecular weights of all gases must occupy equal volumes when under the same conditions, or, in other words, that their molecular weights must be in the same proportion as their densities. If, then, we know the density of a gas or vapour, whether simple or compound, we can at once find its molecular weight, and conversely, if we know its molecular weight its density may be easily calculated.

The molecular weight of hydrogen, which consists of two atoms and has therefore the relative weight 2, is taken as the normal volume, and is said to occupy two volumes. The molecular weight of every other gaseous substance will therefore also occupy two volumes under the same physical conditions, and to this law there are very few exceptions. The molecular weight of oxygen is 16×2, and this gas should therefore be 16 times as heavy as hydrogen, which agrees with experiment (sp. gr. of hydrogen $= 0{\cdot}0692$; sp. gr. of oxygen $= 1{\cdot}1056 = 16 \times 0{\cdot}0692$). Similarly, the molecular weight

[1] Introduced by the Editor.

of water, consisting of two atoms of hydrogen and one of oxygen, is $2 \times 1 + 16 = 18$, whence water gas should be $\frac{18}{2} = 9$ times as heavy as hydrogen; and, finally, the molecular weight of hydrochloric acid, consisting of one atom of hydrogen and one of chlorine, is $1 + 35{\cdot}5 = 36{\cdot}5$, the gas should therefore be $\frac{36{\cdot}5}{2} = 18{\cdot}25$ times as heavy as hydrogen. These and innumerable other results also agree closely with experimental determinations.

Further, the weight of a litre of hydrogen being known (0·0895 gramme at 0° and 760 mm.), we can easily find the weight of a litre of any other gas at the normal temperature and pressure, provided we are acquainted with its molecular weight. Thus the weight of a litre of oxygen under normal conditions is $0{\cdot}0895 \times \frac{32}{2} = 1{\cdot}432$ gramme; of water-gas, $0{\cdot}0895 \times \frac{18}{2} = 0{\cdot}806$ gramme; of hydrochloric acid gas, $0{\cdot}0895 \times \frac{36{\cdot}5}{2} = 1{\cdot}633$ gramme.

The densities of gases and vapours are usually compared with that of air as a standard—*i.e.* the density of air is taken as unity In order to find from these densities the various molecular weights we must multiply by 14·44, which is the relative density of air compared with hydrogen $\left(\frac{1}{0{\cdot}0692}\right)$, and again by 2, because this is the molecular weight of hydrogen. In other words, we multiply by 28·88. The density of water gas, for example, is 0·622, and its molecular weight $0{\cdot}622 \times 28{\cdot}88 = 17{\cdot}96$, or the same as its theoretical molecular weight.[1]

CHEMICAL AFFINITY AND UPON WHAT IT DEPENDS.

The chemical force of attraction (affinity) which resides in the atoms of the elements is of different strength. For example, the affinity of potassium for chlorine is so much greater than it is for iodine, that if chlorine is led into a solution of potassium iodide

[1] For a more detailed account of Avogadro's law, the student is referred to the Appendix.—ED.

the chlorine unites with the potassium, and all the iodine is set free. In the same manner, the affinity of iron for chlorine is so much greater than that of copper, that if a bright rod of iron is placed in a solution of copper chloride, it becomes at once covered with a coating of metallic copper, and at last all the copper is separated out from the compound in the metallic form, while an equivalent quantity of iron unites with the chlorine which was previously combined with the copper.

But, it may be asked, *How* much greater is the affinity of potassium for chlorine than for iodine, or of chlorine for iron than for copper? And it might be thought that the experimental answers to such questions ought not to be more difficult than the measurement of the force of gravity, the strength of an electric current, and other physical forces. But chemistry is in this respect far behind physics, and not only because chemistry is a younger science, but also because chemical affinity is largely influenced by a number of important conditions which often occur together—by temperature, light, electricity, state of aggregation, quantity, &c., and which often cause a powerful affinity to be weakened, and a weak affinity to be strengthened. Some examples of this may serve to show how difficult it is to determine the force of these oft-changing chemical affinities.

Influence of Temperature on Chemical Affinity.

At the ordinary temperature, mercury and oxygen do not possess sufficient affinity to combine with one another, nor is their affinity strong enough to produce this change at the boiling-point of water; but at a temperature of about 300° they unite chemically with one another, and form red oxide of mercury. This compound is, however, again decomposed into its constituents at a slightly higher temperature (under 400°). At 400° mercury and oxygen have as little affinity for one another as at the ordinary temperature. The metal potassium, when moderately heated in a stream of carbonic acid gas, abstracts the oxygen from this compound to form an oxide, and then a carbonate, charcoal being separated. But if potassium carbonate is heated with charcoal up to bright redness, the affinity of the charcoal for the oxygen becomes greater than that of the metal for the same element, and the potassium is again set free. Charcoal, which at the ordinary temperature has a very weak affinity for oxygen, obtains the most powerful affinity for this element at a red heat.

Influence of Light on Chemical Affinity.

A mixture of about equal volumes of hydrogen and chlorine, when quite excluded from the light, remains unchanged, and from this we conclude that the atoms of these elements in their molecules do not possess sufficient affinity to combine with one another. But if the mixture is exposed to light, the combination of the two gases, producing hydrochloric acid, goes on the more quickly the more intense the light. It is, further, principally the violet rays of light which produce this chemical change; and these rays are therefore called the *chemically active (actinic) rays.* If the mixture contains pure hydrogen and pure chlorine in exactly equal volumes, diffused daylight produces instantaneous combination. Light is thus able to awaken the affinity of hydrogen and chlorine for one another, and so to cause them to combine. On the other hand, stable compounds—*e.g.* those of silver with chlorine or bromine—are sometimes decomposed by light. We thus see that light also can cause both chemical combination and decomposition.

Influence of the State of Aggregation and of Quantity (Mass) on Chemical Affinity.

Potash has a stronger affinity for sulphuric acid than lime, and sulphuric acid has a stronger affinity for bases than acetic acid; but notwithstanding this, if we mix a solution of potassium sulphate with one of calcium acetate, calcium sulphate separates out and potassium acetate remains in solution. In this case it is the insolubility of calcium sulphate (which is nearly insoluble in water) that causes the stronger acid (sulphuric acid) to separate itself from the stronger base—potash—and to unite with the lime.

In the same manner, the quantities or masses of different bodies acting upon one another also influence chemical changes. Sulphuric acid has a much stronger affinity for metallic oxides than hydrochloric acid, still the latter can partially displace the former in solutions of the sulphates, and the more completely the more it is in excess. If, for example, strong hydrochloric acid in considerable quantity is added to the blue aqueous solution of copper sulphate, free sulphuric acid is obtained with copper chloride, the latter being easily recognized by the green colour which the blue solution gradually acquires.

These examples suffice to show that the force of chemical

affinity residing in the atoms of the element is difficult to measure, since it is influenced and changed in very various ways by other secondary forces and conditions. Before we are in a position to measure accurately the strength of these secondary forces, even when several act together, we shall not be in a position to predict accurately and to calculate mathematically what would be the result when substances, acting chemically upon one another, are brought into contact under different conditions; although this is always the ultimate goal of all chemical investigation.

But as long as we remain far distant from this end, as at present, chemistry is a science in which mathematical calculations can be little used.[1]

CHEMICAL NOMENCLATURE.

The impossibility of inventing empirical names for many thousand chemical compounds has been long admitted, and at an early date it was proposed to form the names so that everyone might easily understand the nature of any particular compound, and to what class it belonged, by the name given to it.

But besides these rational designations, other empirical names, which come to us with the authority of age, and which also possess the merit of being shorter, are still employed, especially by those unacquainted with the principles of chemistry. The chemist occasionally makes use of the names: soda, potash, Glauber's salts, lunar caustic, &c., although in inorganic chemistry such names are but little employed. In organic chemistry, on the other hand, where we have to refer to whole classes of bodies, of whose chemical composition we know but little, as sugar, starch, the glucosides, &c., we must content ourselves for the present with the empirical names.

[1] Other things being equal, the strength of the affinity which causes two substances to unite with one another is proportional to the quantity of heat set free on their combination. 'The quantity of heat evolved when a molecule of any compound is produced under the same physical conditions is always the same, and if certain changes are possible among a system of bodies, that change will take place which produces the greatest amount of heat.' Thus, if two elements, A and B, are mixed with a third, C, with which each can unite directly, combination will take place between those two which liberate the greater quantity of heat on their union.—ED.

The compounds produced by the union of the elements, and of these compounds again combined together, mostly belong to three classes—*bases*, *acids*, and *salts*. The compounds of oxygen with the other elements, the most numerous of all, are called *oxides*; in the same manner, those of sulphur are *sulphides*, those of chlorine are *chlorides*, of bromine *bromides*, &c.

The oxides may be divided into two great classes—*basic oxides* and *acid oxides*; those not belonging to either of these classes are mostly indifferent compounds.

Those oxides which have a basic character—*i.e.* which combine with acids to form salts—may be called the oxides proper, and their name is built up from the name of the element with which the oxygen is combined. Thus we say potassium oxide, zinc oxide, &c.

In some cases we are acquainted with *two* basic oxides of an element. We know, for example, two basic oxides of copper, iron, mercury, and other metals. In order to clearly distinguish these from one another, the termination of the metal is changed; the termination *-ic* is added to the metal to indicate the compound containing the greater quantity of oxygen, and the termination *-ous* to indicate the compound containing the smaller quantity of oxygen. Thus we say mercuric oxide and mercurous oxide. In cases where these terminations when added to the name of the metal would be harsh, the Latin name of the metal is employed: we say, for example, ferric oxide and ferrous oxide for the two oxides of iron, cupric oxide and cuprous oxide for those of copper, &c.

Those basic oxides, as ferric oxide, chromic oxide, which contain the atoms of the metal, and oxygen in the proportion of two to three, are often called *sesqui-oxides*, or one-and-a-half oxides.

Oxides of the metals, which possess neither acid nor basic character, and which contain *more* oxygen than the basic oxide, are called *peroxides*. We are acquainted, for example, with manganese peroxide, lead peroxide, &c. They give up the excess of oxygen which they contain when heated with strong acids.

Suboxides, of which the number is very small, are the indifferent oxides of the metals which contain less oxygen than the basic oxides. On treatment with acids they yield the metal and the basic oxide, which is richer in oxygen. Such an oxide is lead suboxide.

The oxygen compounds which are said to have an acid character, and are sometimes called acids, are those which unite with

bases to form the ordinary or oxygen salts. They form with water the true *oxy-acids*, and are called *anhydrides*. The names are built up in the same way as those of the oxides, except that the termination *-ic* is always added if there be only one compound of the element with oxygen. Thus, the single oxide of carbon of an acid character is called carbonic anhydride.

We further distinguish between those anhydrides of the same element which contain different quantities of oxygen by the same terminations as are used for the oxides (*-ic* and *-ous*); for example, the two anhydrides of sulphur are sulphuric anhydride and sulphurous anhydride; of nitrogen, nitric anhydride and nitrous anhydride.

Some elements—*e.g.* chlorine—are capable of forming a larger number of oxides with acid characteristics. These are distinguished by the prefixes *per-* and *hypo-*. The oxide which contains more oxygen than chloric anhydride is called perchloric anhydride, that which contains less than chlorous anhydride is called hypochlorous anhydride.

The oxy-salts are named from the bases and acids of which they consist. Salts formed from acids with the termination *-ic*, have the termination *-ate*, while those from acids with the termination *-ous* end in *-ite*. For example, potassium sulphate is the compound of potassium oxide and sulphuric acid; cupric nitrate, of cupric oxide and nitric acid; mercurous nitrite, of mercurous oxide and nitrous acid.

The name hydrate includes two classes of bodies: the acid hydrates, the oxy-acids, &c., and the basic hydrates, the hydrates proper. (See Appendix.) The *acid hydrates*, or as they are better called *acids*, and which are produced by the union of the anhydrides with water, usually contain in their molecule the same number of hydrogen atoms as the normal salt of a monad metal contains of a metal.[1] The names of the acids are derived from those of the corresponding anhydrides; thus, from sulphuric anhydride we get sulphuric acid, from phosphoric anhydride phosphoric acid, &c.

Basic hydrates (see Appendix) are the oxides of the metals in which a portion of the metal is displaced by hydrogen—*e.g.* potassium hydrate, cupric hydrate. They are often produced by

[1] An acid is therefore a hydrogen salt, and the hydrogen which can be displaced by a metal, not necessarily all which the acid contains, is called its *displaceable hydrogen*. Accordingly, as an acid contains one, two, three, &c., atoms of displaceable hydrogen, it is said to be *mono-*, *di-*, *tribasic*, &c.—ED.

the union of the basic oxides with water, and may be considered, as was formerly the case, as compounds of these two substances.

The chemical nomenclature of the acids, bases, and salts, which contain sulphur instead of oxygen is not so well developed, and probably because we are less accurately acquainted with these compounds. They may be called *sulpho-acids*, *sulpho-bases*, and *sulpho-salts*. On the union of a sulpho-acid (*e.g.* carbon disulphide or arsenious sulphide) with a sulpho-base (*e.g.* potassium sulphide or sodium sulphide) a sulpho-salt is produced. Thus carbon disulphide (sulpho-carbonic acid) with sodium sulphide gives sodium sulpho-carbonate; arsenious sulphide (sulph-arsenious acid) with potassium sulphide gives potassium sulph-arsenite, and in this way all other sulpho-compounds are distinguished.

The salts which result from the direct union of the halogen elements (chlorine, bromine, iodine, and fluorine) with the metals, and which contain neither oxygen nor sulphur, are called the *haloid-salts*, and the corresponding acids, containing hydrogen in the place of the metal, are the *haloid-acids*.

Hydrochloric acid, the compound of hydrogen and chlorine, is not to be confused with chloric acid, which contains oxygen as well as these elements.

The metals unite with the halogens usually in the same proportion as with oxygen, and the corresponding names are the same. To mercuric oxide corresponds mercuric chloride, containing a quantity of chlorine equivalent to the oxygen in the oxide; similarly, mercurous chloride corresponds to mercurous oxide.

In cases when elements unite with the halogens in more than two proportions, or when, as in the case of phosphorus, the compounds cannot be included under the true haloid-salts, it is customary to indicate the number of chlorine, bromine, &c., atoms contained in the molecule of the compound by the prefixes *mono-*, *di-*, *tri-*, *tetra-*, *penta-*, *hexa-*, &c. The two compounds of phosphorus and chlorine, which contain respectively five and three atoms of chlorine united to one atom of phosphorus, are called phosphorus pentachloride and phosphorus trichloride; and, in the same manner, we also say carbon disulphide, referring to the compound containing one atom of carbon and two of sulphur in the molecule.

Haloid compounds are also known, in which a portion of the chlorine, bromine, &c., is displaced by oxygen. These are called

oxychlorides, *oxybromides*, &c. To this class belongs the well-known phosphorus oxychloride. Those compounds in which sulphur displaces a portion of the halogen instead of oxygen are similarly designated—*e.g.* the compound of phosphorus, chlorine, and sulphur is called phosphorus sulphochloride.

Alloys are the intimate mechanical mixtures produced by melting metals together. Those alloys which contain mercury are called *amalgams*. Alloys and amalgams can only be produced from metals.

CHEMICAL SYMBOLS AND FORMULÆ.

When we calculate with figures we do not use the words representing them, but their signs. In the same manner, the need of symbols to express chemical substances, and by a suitable combination of these symbols to reproduce chemical thoughts in a brief but general manner, was early recognized in chemistry.

It is customary to represent the elements by letters and to express chemical compounds by the juxtaposition of these letters. The symbol H has been chosen to represent the element hydrogen, and I the element iodine; by placing these symbols together, without any sign between them, the compound of the two elements —hydriodic acid—is represented (HI). In the same way the compound symbol CaO is a simple expression for the compound of the metal calcium (Ca) with the gas oxygen (O)—*i.e.* common quick-lime.

The symbols of the elements are the first letter of their names and usually of their Latin names: thus K represents potassium (kalium), C = carbon, &c. When the names of several elements begin with the same letter, some other letter is added: thus B means boron, Ba = barium, Br = bromine, Mg = magnesium, Cd = cadmium, Ag = silver (argentum), Hg = mercury (hydrargyrum), Fe = iron (ferrum), Sn = tin (stannum), &c.

But the chemical symbols of the elements have another and more important meaning. The symbol HI does not only indicate the presence of hydrogen and iodine, but expresses also the quantities by weight of the constituents of hydriodic acid which are contained in its molecule. The symbol H indicates one atom of hydrogen, or the smallest weight which enters into a chemical

compound (which is taken as unity), and, in the same manner, I means one atom of iodine or 127 parts by weight; while, finally, the compound symbol HI expresses the compound of hydrogen and iodine, which contains one part of the former united with 127 parts of the latter, and of which the molecular weight is, therefore, $127 + 1 = 128$.

The accompanying table on p. 60 gives the names of the elements, alphabetically arranged, with their symbols and atomic weights, the non-metallic elements being in *italics*.

Since, however, the elements combine with one another not only in simple but also in multiple proportions, and as this must also be represented by chemical symbols, it is customary to express the number of atoms of the one element which unites with the other to form a molecule by a small figure placed to the right of the symbol of the element. For example, SO_2 means the compound of one atom (32 parts) of sulphur with two atoms (2×16 parts) of oxygen, and the formula H_2O means the compound produced by the union of two atoms of hydrogen (2 parts) with one atom of oxygen (16 parts).

The figures placed to the right of any chemical symbol refer only to this one symbol, but another large figure placed on the left of a symbol multiplies all that follows up to a comma, full-stop, or plus sign. The formula $2KCl,PtCl_4$, for example, represents the compound of two atoms of potassium, and two atoms of chlorine (or two molecules of potassium chloride), with one of platinic chloride. Similarly, the formula $SO_2\left\{\begin{matrix}ONa\\ONa\end{matrix}\right. + 10H_2O$ is the symbolic expression for a compound of sodium sulphate with 10 molecules of water—*i.e.* with 20 atoms of hydrogen and 10 atoms of oxygen.

Every such formula is full of hidden meaning to the chemist. The composition of the above compound (Glauber's salts) might be more briefly expressed by the formula $SNa_2H_{20}O_{14}$, but this only tells us that one molecule contains one atom of sulphur, two of sodium, twenty of hydrogen, and fourteen of oxygen. If we wished to express the fact that ten molecules of water are contained in each molecule of the salt, we might write its formula $SO_4Na_2 + 10H_2O$. But the above formula, $SO_2\left\{\begin{matrix}ONa\\ONa\end{matrix}\right. + 10H_2O$, in which the constituents of the compound are still further arranged, expresses the fact that the four oxygen atoms in the sodium sul-

TABLE OF ATOMIC WEIGHTS.

Name	Symbol	Atomic weight[1]	Name	Symbol	Atomic weight[1]
Aluminium	Al	27·1	Nickel	Ni	58·6
Antimony	*Sb*	120·2	*Niobium*	*Nb*	94
Arsenic	*As*	75	*Nitrogen*	*N*	14·1
Barium	Ba	137	Osmium	Os	190·3
Beryllium	Be	9·1	*Oxygen*	*O*	16
Bismuth	Bi	208	Palladium	Pd	106·4
Boron	*B*	11	*Phosphorus*	*P*	31
Bromine	*Br*	80	Platinum	Pt	194·3
Cadmium	Cd	112	Potassium	K	39·1
Caesium	Cs	132·9	Rhodium	Rh	102·7
Calcium	Ca	40·1	Rubidium	Rb	85·4
Carbon	*C*	12	Ruthenium	Ru	101·4
Cerium	Ce	140·3	Samarium	Sm	(?) 150
Chlorine	*Cl*	35·5	Scandium	Sc	44
Chromium	Cr	52·2	*Selenium*	*Se*	79
Cobalt	Co	58·6	*Silicon*	*Si*	28·3
Copper	Cu	63·4	Silver	Ag	108
Didymium	Di	(?) 146	Sodium	Na	23·1
Erbium	Er	166	Strontium	Sr	87·5
Fluorine	*F*	19	*Sulphur*	*S*	32·1
Gallium	Ga	69·8	*Tantalum*	*Ta*	182
Germanium	Ge	72·3	*Tellurium*	*Te*	(?) 127·6
Gold	Au	196·6	Terbium	Tr	(?) 148
Hydrogen	*H*	1	Thallium	Tl	204
Indium	In	113·7	Thorium	Th	232·5
Iodine	*I*	126·8	Tin	Sn	118
Iridium	Ir	192·5	*Titanium*	*Ti*	48·2
Iron	Fe	56	*Tungsten*	*W*	184
Lanthanum	La	(?) 139	Uranium	U	240
Lead	Pb	206·5	*Vanadium*	*V*	51·3
Lithium	Li	7	Yttrium	Y	89
Magnesium	Mg	24	Ytterbium	Yb	173
Manganese	Mn	55	Zinc	Zn	65·3
Mercury	Hg	200	Zirconium	Zr	90
Molybdenum	*Mo*	96			

[1] See last paragraph on p. 582.

phate perform different functions. Two of them are considered to be in closer connection with the atom of sulphur than the other two. These two atoms of oxygen saturate four of the bonds of the hexad sulphur atom, producing a diad group of elements (SO_2) which is capable of playing the part of a single element, and which is called a *compound radical*. There is another fact expressed in this formula—viz. that this diad radical does not unite directly with the two atoms of sodium, but through the intervention of the other two atoms of oxygen, which have, therefore, other functions than the two former atoms of this element.

The employment of chemical symbols makes the meaning of chemical decompositions much more easy to understand. And the use of formulæ enables us to determine what quantity of a body is necessary to produce, either alone or by its action on a second substance, a given quantity of a third.

We have seen (p. 12) that potassium chlorate breaks up on heating into potassium chloride and oxygen. In order to find out how much of these two substances would be obtained from 100 grammes of potassium chlorate, we must first know the molecular weight of this salt, and how many atoms of each of its elements are contained in its molecule. We could, of course, express this in words, and say one molecule of potassium chlorate consists of one atom of potassium, one of chlorine and three of oxygen, and, the atomic weights of these elements being known, that one molecule of the salt contains :—

35·5 × 1	=	35·5	parts by weight of		chlorine,
39·0 × 1	=	39·0	”	”	potassium,
16 × 3	=	48·0	”	”	oxygen,
		122·5	”	”	potassium chlorate,

which means that on the decomposition of 122·5 parts by weight of potassium chlorate 48 parts of oxygen would be given off, and 74·5 parts of potassium chloride would remain behind.

But all this, which is expressed by so many words, may be at once represented by the simple chemical equation :—

$$ClO_3K = KCl + 3O.$$

Cl means 35·5 parts by weight of chlorine, 3O means $3 \times 16 = 48$ parts of oxygen, and K 39 parts of potassium. Placing these numbers opposite the symbols we get :—

$$\begin{array}{rcll} ClO_3K & = & KCl & + \ 3O, \\ 35{\cdot}5 + 48 + 39 & = & (39 + 35{\cdot}5) & + \ 48, \\ 122{\cdot}5 & = & 74{\cdot}5 & + \ 48, \end{array}$$

which shows that 122·5 parts by weight (grammes, &c.) of potassium chlorate yield 74·5 parts (grammes, &c.) of potassium chloride, and 48 parts (grammes, &c.) of oxygen. From 100 grammes of potassium chlorate we should, therefore, obtain the weights of potassium chloride (x) and oxygen (y) expressed in the two following simple rule-of-three sums :—

$122{\cdot}5 : 74{\cdot}5 :: 100 : x \therefore x = 60{\cdot}8$ grammes potassium chloride.
$122{\cdot}5 : 48 :: 100 : y \therefore y = 39{\cdot}2$ grammes oxygen.

This simple method gives a ready means of calculating the *weight* of any particular substance which can be obtained from a given weight of some other substance in a known chemical reaction. Suppose, however, we wish to know the *volume* of the substance produced when it is a gas. Let us take the same example and imagine that it is required to find how many *litres* of oxygen would be produced when 100 grammes of potassium chlorate were completely decomposed. We have seen above that the *weight* of oxygen produced is 39·2 grammes, and we further know that the weight of a litre of oxygen is 16 times that of a litre of hydrogen (the molecule of the former being 16 times as heavy as that of the latter), or, in other words, is $0{\cdot}0895 \times 16 = 1{\cdot}432$ grammes. From this, therefore, it follows that the 39·2 grammes of oxygen will occupy a volume of $\frac{39{\cdot}2}{1{\cdot}432} = 27{\cdot}3$ litres. This is of course the volume of the gas at the normal temperature (0° C.) and under the normal pressure (760 mm.). In the same manner the volume of any given weight of a gas (and the converse) may be easily found, provided we know its molecular weight.

It has been previously stated (p. 9) that manganese peroxide when heated gives off oxygen. The process, which has been shown by analytical experiments to be according to the following equation, is somewhat less simple. From this equation—

$$3MnO_2 = Mn_3O_4 + O_2,$$

we learn that three molecules (261 parts by weight) of the peroxide yield one molecule (229 parts) of trimanganic tetroxide, and one molecule (32 parts) of oxygen. Whence it follows that 12·2 kilos. of oxygen will be obtained from 100 kilos. of the peroxide.

The chemical manufacturer who wishes to convert 100 kilos. of

saltpetre (potassium nitrate) into nitric acid, so as to obtain the largest yield of acid possible, and to use the smallest quantity of sulphuric acid necessary, must of course know the details of the process he is about to employ, and must remember that acid potassium sulphate is obtained as a bye-product. The reaction which takes place is expressed by the following equation :—

$$\underset{\text{Potassium nitrate}}{NO_2 \cdot OK} + \underset{\text{Sulphuric acid}}{SO_2\begin{cases}OH\\OH\end{cases}} = \underset{\text{Acid potassium sulphate}}{SO_2\begin{cases}OH\\OK\end{cases}} + \underset{\text{Nitric acid}}{NO_2 \cdot OH.}$$

Translating the formulæ into numbers we get—

N = 14	S = 32	S = 32	N = 14
3O = 48	4O = 64	4O = 64	3O = 48
K = 39	H_2 = 2	K = 39	H = 1
		H = 1	
101	98	136	63

which show that the manufacturer must use 98 kilos. of sulphuric acid for every 101 kilos. of saltpetre, and that he will obtain 136 kilos. of acid potassium sulphate and 63 kilos. of nitric acid.

GENERAL REMARKS ON THE CHEMICAL ELEMENTS.

It is remarkable that the elementary constituents of the earth, of which we know more than seventy, occur both in the free state and combined in very different quantities and are very differently distributed on the earth. Some may be found everywhere, others occur rarely and in small quantities ; while others, again, are found only in a few places, but then in considerable quantities. The most widely distributed elements are oxygen, silicon, aluminium, iron, and calcium ; those which are more scarce include the noble metals gold, platinum, &c. Others, which only occur in definite places, but then in considerable quantities, are such as mercury, tin, &c. Finally, some are so rare that we only possess a very meagre knowledge of them and their compounds—*e.g.* indium, caesium.

Some elements occur as such free in nature, or, as it is said, *native*—*e.g.* platinum—but the majority of the elements are found

exclusively in combination with others; while some, as sulphur, oxygen, nitrogen, silver, copper, occur both free and combined.

A question which has often been asked but never answered, and perhaps never will be, is whether the interior of the earth may not contain other elements besides those with which we are acquainted, and whether the elements and their compounds may not be differently distributed there than they are in the portion of the earth's crust accessible to us.

The portion of the earth which we can investigate—*i.e.* the atmosphere, the ocean, and a very thin layer of the solid crust—is only a minute fraction of the whole mass. The mean radius of the earth is over 3,950 miles, and as we descend towards the centre the temperature increases to such an extent that at a depth of about fifty miles nearly all the substances we know on the earth would be in a liquid state. That this is the case in some places is proved by the existence of volcanoes which at times pour forth streams of liquid lava. But it must not be forgotten that the substances forming the interior of the earth are under a much greater pressure than those at the surface, and we cannot tell how far the effect of this pressure would modify the melting-points of the different bodies. It may be considered as probable that the interior of the earth consists of substances heavier than those at the surface, for while the mean specific gravity of the rocks at the surface is between 2·5 and 3·0, that of the entire earth is about 5·5. But here again pressure would tend to compress the substances in the interior and so to make them heavier; for example, at the ordinary temperature, water would become as heavy as mercury at a depth of 360 miles. How far these two opposing forces, that of the internal heat and that of pressure, counterbalance one another remains, and probably will remain, an unsolved problem for us.

But it is certainly to be expected that many unknown elements are hidden in the interior of the earth, perhaps some even heavier than platinum and iridium, which, owing to their high specific gravity, can never approach the earth's surface; while, on the other hand, it may be mentioned that numerous analyses of meteorites which have fallen to the earth from extra-terrestrial space have not revealed any new elements to us.

We consider the present chemical elements to be simple bodies because we are not able at present to further decompose them

(p. 5), but we do not therefore think them incapable of decomposition. On the contrary, the suspicion that many of them are either compound bodies or modifications of one element is supported by weighty reasons.

In the first place, the history of chemistry teaches us that substances long considered as elements can be broken up by improvements in the methods and means of decomposition into simpler bodies, and now it is thought possible that even these may be compounds.

Potassium hydrate, a compound of potassium, oxygen, and hydrogen, quick-lime, consisting of calcium and oxygen, and other bodies, were thought to be elements at the beginning of the present century, when the electric current as a powerful means for effecting decomposition was still unknown. By electrolysis the unknown metal potassium was recognized as a constituent of potassium hydrate, and the metal calcium was isolated from quick-lime. Such events justify the expectation that with the discovery of new and more powerful means of decomposition, many of the elements would disappear from the present list.

Compound bodies are known, the compounds of which have so close an analogy to the similar compounds of certain elements that it is often difficult to separate them from one another. Such compounds would certainly have been classed with the elements had not their decomposition been accomplished. Of these, *cyanogen*, a compound of carbon and nitrogen, is a striking example. The compounds of this substance with the metals and with hydrogen closely resemble the similar compounds of the elements chlorine, bromine, and iodine. And this similarity makes it quite possible that chlorine, bromine, and iodine will, some time or other, prove to be compounds.

Besides chlorine, bromine, and iodine, other elements exist which possess remarkable similarity in their compounds. Such are, for example, the groups: sulphur, selenium, and tellurium; potassium, sodium, and lithium; barium, strontium, and calcium. It is certain that these similarities are just as little accidental as the fact that the similar elements generally occur associated together in nature.

Still more remarkable are the relations in which the atomic weights of the elements of each group stand to one another. The atomic weight of the middle element is almost exactly the mean of those of the other two. For example, in the group potassium,

sodium, and lithium, with the atomic weights 39, 23, 7 respectively, the mean of 39 and 7, or $\frac{39+7}{2}$, is exactly 23—*i.e.* the atomic weight of sodium. Similarly in the second group, barium (137), strontium (87·5), and calcium (40), the mean of 137 and 40 is 88·5, or very nearly the atomic weight of strontium; in the same manner in the third, chlorine (35·5), bromine (80), and iodine (127), the mean of 35·5 and 127 (81·25) nearly coincides with the atomic weight of bromine (80); and finally, in the fourth group: sulphur (32), selenium (79), and tellurium (128), the mean of the atomic weights of sulphur and tellurium is 80, or very nearly the same as the atomic weight of selenium (79). It will be noticed that the numbers do not exactly agree, although they very nearly do so.

It is certainly not accidental that the members of these *natural groups* and other similar ones always occur together in nature, that they have a close chemical likeness to one another, and that such a remarkable relation connects their atomic weights together. We do not know the cause and connexion of these facts; we can only guess and surmise that truths lie hidden in them which, if brought to light, would considerably enrich and further our science.

The investigator cannot attempt to explain every fact, even those close at hand, and must beware of substituting speculation for experiment. Much might be written on facts such as those to which we have referred, and brilliant hypotheses might be built upon them; but these theories often lose their splendour when experimental investigation lifts the veil and discloses the truth.

As might be expected from the great divergence in the atomic weights, similar groups can be easily built up from other elements than those mentioned above. The atomic weights of oxygen, nitrogen, and carbon offer an example. The mean of the atomic weights of oxygen (16) and carbon (12) is 14, or exactly the atomic weight of nitrogen. Still no one would think of placing these elements together in a group because of the great difference in their chemical behaviour. The compounds of oxygen, nitrogen, and carbon with other elements—*e.g.* with hydrogen—have not the slightest resemblance to one another; they may in fact be said to differ from one another as much as the hydrogen compounds of the natural group chlorine, bromine, and iodine resemble one another. These three elements cannot, therefore, be grouped

together in the same manner as chlorine, bromine, and iodine, &c. : the connexion between their atomic weights appears to be purely accidental.

Remarkable relations between the elements are also found in another direction. There are certain elements of which the atomic weights are almost exactly the same, and which always occur associated together in nature. To these belong the metals platinum and iridium, with nearly the same atomic weight (195 and 193) ; rhodium and ruthenium (104) ; cobalt and nickel, with the atomic weights 59 and 58·5 ; and iron and manganese (56 and 55), as well as some others.

These facts obtain increased importance since those elements, which occur together in nature and possess about the same atomic weight, always exhibit a close relation in their chemical properties. And since we know that elements exist which, though chemically identical, can possess very different physical and even chemical properties (*e.g.* graphite and diamond, both modifications of the element carbon ; ordinary and red or amorphous phosphorus), the supposition is not unsupported that at a later time it may be possible to prove the identity of cobalt and nickel or of iron and manganese, and even to convert the one into the other.

From whichever side the question of the elementary nature of the elements is attacked, it seems probable, although no decided answer can be obtained, that the elements, or the greater part of them, are capable of decomposition and that their number might be much reduced.

PHYSICAL AND CHEMICAL PROPERTIES OF BODIES.

When two bodies are allowed to act upon one another it is easy in most cases to decide whether a chemical change has taken place or not. Sometimes, however, especially in organic chemistry, careful observations and experiments are necessary to decide whether two products of different reactions are identical or different. This is done by an exact determination of the physical and chemical properties of the bodies under investigation, the enumeration of which constitutes their real description.

One of the most important of the *physical properties* of a body is its

State of Aggregation.—It must be known whether the body in question is a solid, a liquid, or a gas under normal conditions, and whether it changes its state of aggregation, and if so, under what conditions. If the body is a liquid, its boiling-point, reduced to the normal atmospheric pressure, must next be determined, as well as the temperature at which the liquid becomes solid, if at all, or its freezing-point (melting-point). If the substance is a gas, the temperature, or pressure, or both, under which it becomes liquid must be found. With solid bodies the determination of the temperature at which it becomes liquid (melting-point) must be made.

The *colour* of the substance must also be noticed; it often changes with the state of aggregation. Sulphur, for example, in the solid state is bright yellow, in the liquid state yellow to brown, in the gaseous state reddish-brown; iodine, at the ordinary temperature, is a dark-grey solid with metallic lustre, but when melted it becomes reddish-brown, and in the gaseous state has a splendid violet colour.

The *taste* and *odour.*—The determination of these properties, especially the former, require caution, owing to the poisonous nature of many substances, and because of the caustic action of others —*e.g.* sulphuric acid, caustic potash—on the mucous membrane of the tongue and mouth. A large number of volatile bodies may be easily and tolerably certainly recognized by their odour alone—*e.g.* chlorine, iodine, sulphurous acid, chloroform, carbon disulphide, camphor. We distinguish different tastes as: acid (sour), alkaline (soapy), acrid, astringent, sweet, bitter, insipid, &c.; and different odours as: acid, putrid, suffocating, &c. The odour of bodies is often compared with that of other well-known substances; thus, we say an ethereal odour, or that a body smells like cinnamon, bitter almonds, camphor, butyric acid, &c.

Lustre, Fracture, and Hardness.—Among solids, different kinds of lustre of their surfaces are distinguished according to substances whose lustre is well known—*e.g.* metallic lustre, diamond lustre, vitreous lustre, silky, mother-of-pearl lustre, &c.

The fracture of a solid when broken is indicated by the same terms as the lustre. Some bodies have a crystalline fracture, others a conchoidal (shell-like), or a splintery fracture. The crystalline fracture may be laminated, granular, or fibrous.

For the determination of the hardness of solids, the same series of minerals is used as in mineralogy. This scale consists of a series of ten minerals of different degrees of hardness, commencing with the diamond and ending with talc. Liquids are distinguished as viscid and mobile. It often happens that viscid liquids are heavy—*e.g.* concentrated sulphuric acid—and that mobile liquids are light, although the greater or less consistency of the liquid does not depend upon its specific gravity. The heavy liquid chloroform is very mobile, while the light fatty oils are viscid.

The *specific gravity* or *density* of a substance indicates how many times heavier the substance is than some other known body. Water is chosen as the unit for liquids and solids, air as the unit for gases and vapours.

A piece of iron weighed in the air is much heavier than when dipped in water. In the latter case its loss in weight is exactly the weight of the water which it displaces. The absolute weight of the iron divided by the weight of the water displaced (its own volume) gives the specific gravity of iron (7·8). Similarly determined, the specific gravity of platinum is nearly three times as much (21·5).

If we take a small vessel, of known weight, with a narrow neck on which is a mark, fill it with mercury and weigh it, and then do the same with water, we obtain, on subtracting the weight of the flask from each weighing, the relative weights of mercury and water (equal volumes), and, dividing the former by the latter, the specific gravity of mercury (13·6) is found.

In a similar manner the specific gravities of gases and vapours may be obtained, employing the word vapour for the gases produced on heating volatile liquids above their boiling-points.

The methods by which determinations of specific gravity are made, especially those of gases and vapours, are taught in physics. In order to thoroughly understand them, the student should make determinations himself in the chemical or physical laboratory. The determination of the density of a compound in the gaseous state (its vapour density) is of the greatest importance, since this density when multiplied by 28·88 gives the molecular weight of the compound (p. 51).

Every substance possesses its own peculiar specific gravity, which is always the same, under the same conditions (particularly temperature and pressure), however the substance occurs or however it may have been obtained. A substance which from its pro-

perties we might take for iron, but which has a different specific gravity, say 9 instead of 7·8, is not iron. Numerous compounds exist in organic chemistry which not only possess the same percentage composition, but are also so similar in their chemical properties and behaviour that they might be thought to be identical if the specific gravity of their gases were not so different from one another, which proves that they are polymeric and not identical bodies.

One of the most important of the physical properties of a body is its capacity for heat or its *specific heat.* This must be carefully determined by one of the various methods known to physicists. The specific heat is particularly important in the case of solids, and it has been found that if the solid be an elementary body, the product of its specific heat into its atomic weight is a constant quantity (about 6). This may be expressed in another way by saying that the capacity for heat of all elementary atoms in the solid state is the same—*i.e.* the quantity of heat required to raise atomic weights of different solid elements to the same temperature from 0° C. (*atomic heat*) is a constant quantity. The law is known as *Dulong and Petit's* law.[1]

Crystalline Shape.[2]

When a substance passes from the liquid or gaseous to the solid state, its molecules generally arrange themselves so that regular symmetrical forms or crystals are produced. These forms are always the same for one and the same substance when produced under similar conditions, and even when the conditions producing the crystals vary the form is usually the same.

Common salt, sal-ammoniac, and alum under all conditions crystallize in the regular system ; sulphur crystallizes in two forms, but only two, accordingly as the crystals are produced from a solution or from the liquid substance by allowing it to cool.

The plane surfaces composing the regular shapes of crystals are called *faces* ; the inclination of any two faces to one another is called the *angle* between the faces. It is a remarkable fact that although the shape of two crystals of the same substance, prepared in the same manner, may apparently be very different from one

[1] Introduced by the Editor. A fuller account of this law is given in the Appendix.

[2] This short sketch has been introduced by the Editor.

another, the *angle* made by any two similar faces always remains unchanged.

It has been found that the faces of crystals can be arranged according to certain imaginary lines supposed to be drawn through the crystal and called its *axes*; and according to the relative length and inclination of these axes all crystals are divided into six systems: the regular, tetragonal, hexagonal, rhombic, monoclinic, and triclinic systems, as they are usually designated.

The Regular System.

In this system there are three axes, which are all equal and all at right angles to one another. The fundamental forms of this

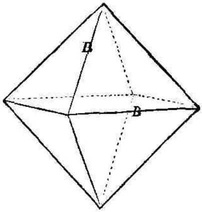

Fig. 16.

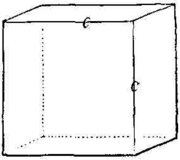

Fig. 17.

system are: the *regular octahedron* (fig. 16), the *cube* (fig. 17), and the *rhombic dodecahedron* (fig. 18). Figs. 19 and 20 illustrate two

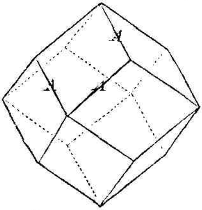

Fig. 18.

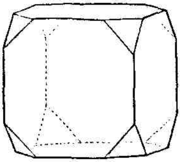

Fig. 19.

common forms of the octahedron and cube combined; in the former the cube predominates, in the latter the octahedron. In these forms all possible faces are developed, and such crystals, by

far the most common, are called *holohedral*. Other forms are, however, known in which only one half or one quarter of the entire number of faces is developed. Such crystals are called

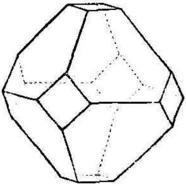

Fig. 20.

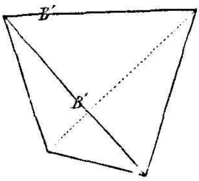

Fig. 21.

hemihedral and *tetrahedral* respectively. The hemihedral form of the octahedron is the *tetrahedron* (fig. 21).

Among the large number of bodies crystallizing in this system,

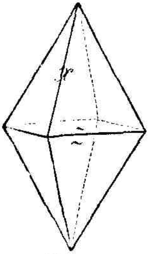

Fig. 22.

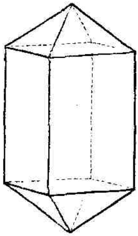

Fig. 23.

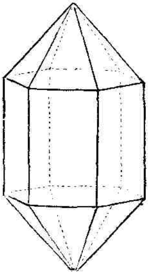

Fig. 24.

the following are common examples: common salt (cubes), alum (octahedra and cubes), fluor-spar, garnet, the spinelles, galena, zinc-blende (often tetrahedra).

The Tetragonal System.

In this system the axes are still all at right angles to one another, but one is different in length to the other two, which are themselves equal. The first axis is the *primary axis*, the other two are the *secondary axes*. The fundamental forms are the *tetragonal*

pyramid (fig. 22) and the *tetragonal prism.* Fig. 23 represents a combination of one of the prisms with the pyramid, a form in which tin-stone often occurs.

Common substances which crystallize in this system are: tin-stone, rutile, potassium ferrocyanide.

The Hexagonal System.

The axes of this system are four in number, which distinguishes it from all other systems. Three of these axes (secondary) are equal in length, lie in the same plane, separated from one another by an angle of 60°, and are all at right angles to the fourth or primary axis, of which the length is different. Fig. 24 shows a combination of the fundamental pyramid and prism—a common form in rock crystal.

The hemihedral forms of this system are very important—many substances (*e.g.* calc-spar) assuming these forms only. Fig. 25 represents the fundamental *rhombohedron*, and fig. 26 a *scalenohedron.*

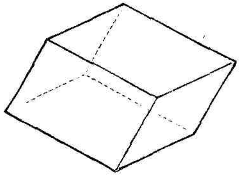

Fig. 25.

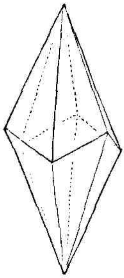

Fig. 26.

A large number of bodies crystallize in the hexagonal system. Among them may be named rock-crystal, apatite, calc-spar, sodium nitrate.

The Rhombic System.

The axes of this system are all of different lengths, but all are at right angles to one another. One axis is chosen as primary axis, and of the other two secondary axes the longer is called the *macro-*

diagonal, and the shorter the *brachy-diagonal*. The two figures 27 and 28 represent the fundamental pyramid and a combination, common in crystals of desmine.

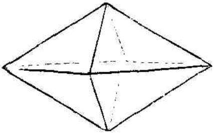

Fig. 27.

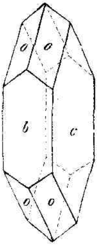

Fig. 28.

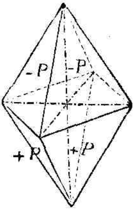

Fig. 29.

This is also a large system; some of the more important substances crystallizing in it are *sulphur, topaz, zinc sulphate.*

The Monoclinic System.

All three axes of this system are of unequal length; of the se ondary axes one (*ortho-diagonal*) is perpendicular to the primary axis, and the other is inclined to it at some angle other than

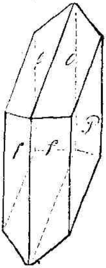

Fig. 30.

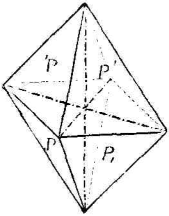

Fig. 31.

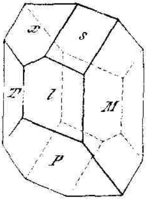

Fig. 32.

90° (*klino-diagonal*). The fundamental pyramid is shown in fig. 29, and a combination (gypsum) in fig. 30.

Of substances belonging to this system may be mentioned:

sulphur (when melted and allowed to cool), gypsum, orthoclase, cane-sugar.

The Triclinic System.

In this system, the most unsymmetrical, all the axes are unequal, and they are all inclined to one another at some other angle than 90°. The two figures (31 and 32) represent the fundamental pyramid and a combination occurring in albite.

Albite, copper sulphate, axinite, and other substances occur in crystals belonging to this system.

Dimorphism.—Substances which, although chemically identical, possess the power of crystallizing in two entirely different forms are said to be *dimorphous*—*e.g.* sulphur (see ante). Some substances (*e.g.* titanic oxide) can crystallize in three different forms and are called *trimorphous.*

Isomorphism.—Two bodies are called *isomorphous* when they crystallize in the same form and possess a similar chemical composition. Thus: calc-spar ($CaCO_3$), dolomite ($CaMgCO_3$), magnesite ($MgCO_3$), spathic iron ore ($FeCO_3$), calamine ($ZnCO_3$) all crystallize in rhombohedra, having nearly the same angle, and a similar chemical composition ($M''CO_3$). Many other examples might be given of this important and useful law.[1]

Numerous methods may be employed to produce crystals from gases, liquids, or amorphous solids. Many gases and liquids on becoming solid by cooling assume a crystalline state. The violet coloured gas of iodine deposits on cooling dark-grey crystals of solid iodine. Water crystallizes—*i.e.* becomes ice—at 0°; liquid carbonic acid at −78°.

Solid bodies, which can be volatilized unchanged, are mostly obtained in a crystalline state by *sublimation*, or by heating the solid and gradually cooling the gas which is evolved. In this manner, sulphur, arsenious acid, mercuric chloride, &c., may easily be crystallized. Most bodies melt before they sublime, others pass directly from the solid into the gaseous state—*i.e.* they boil at a lower temperature than they melt.

Solid bodies which can be melted may be easily made to crystallize by allowing a portion of the liquid to solidify and then pouring off the still liquid portion. Crystals of sulphur, bismuth, &c., may be easily obtained in this way.

The commonest method of preparing crystals is, however, to

[1] See Appendix.

dissolve the substance in some volatile liquid and then allow it to evaporate slowly; common salt crystallizes in cubes from a saturated aqueous solution on evaporation; or a hot saturated solution may be allowed to cool slowly, as a liquid usually dissolves more of a substance when hot than when cold. In this way crystals of nitre, Glauber's salt, and many other salts, are obtained from hot water, sulphur from hot carbon disulphide, mercuric chloride from alcohol, graphite from cast-iron, &c.

Many metals—copper, silver, &c.—may be deposited from their aqueous solutions in a crystalline form by electrolysis. But the conditions under which most of the numerous natural crystals of the mineral kingdom, particularly those which do not dissolve in the ordinary solvents (corund, heavy-spar, and many others), have been produced are as yet unknown.

Solubility.—Nearly all solid bodies dissolve in some liquid; but the manner in which solution takes place may be different. Many liquids dissolve solids without producing any chemical change—thus, common salt, nitre, &c., dissolve in water, and the dissolved substances then separate out again unchanged on the removal of the solvent. This kind of solution may be called *mechanical solution.*

Other liquids dissolve solids by reason of a chemical action which takes place between them. Water dissolves sulphuric anhydride, phosphoric anhydride, barium oxide, &c., to form chemical compounds with these bodies. In other cases chemical change and decomposition may take place, as when nitric acid dissolves lead oxide or metallic copper. This kind of solution, depending upon chemical change, may be called *chemical solution.*

Of mechanical solvents, water is by far the most important; then follow alcohol, ether, carbon disulphide, chloroform, benzol, &c. The solubility generally increases with the temperature, so that liquids at the boiling temperature usually dissolve far more of a solid than at the ordinary temperature of the air. In some cases, *e.g.* common salt in water, such increase of solubility is but very slight (see App.); and a few substances are more soluble at the ordinary temperature than when the liquid is heated, for example, calcium hydrate in water—hence lime-water (a solution of calcium hydrate) becomes milky when warmed from the separated calcium hydrate, which, however, again dissolves on cooling.

Many bodies which are insoluble in water dissolve in alcohol,

ether, &c., and *vice versâ*. Barium chloride and Glauber's salt are soluble in water but insoluble in alcohol and ether, while many organic substances (*e.g.* stearine) are insoluble in water but soluble in alcohol and ether.

It is of great importance in determining the identity or difference of two bodies to know the different quantities dissolved by their solvents at various temperatures. Such determinations may either be referred to the boiling point of the liquid, to 0°, or to the mean temperature.

The Chemical Properties of Bodies.

To these properties belongs the solubility of a substance in different solvents, by which a chemical change is produced. It may be known that chemical action has taken place if, on evaporating the solvent, a chemical compound of the original substance remains behind. No metals are mechanically dissolved by any liquid except mercury. Some are acted on by water and alcohol and dissolved chemically. Most of the metals dissolve chemically in some acid, as nitric, hydrochloric, or sulphuric acid, or in aqua regia. Mercury, copper, lead, &c., are dissolved by nitric acid and converted into nitrates; while tin is transformed into the insoluble dioxide by nitric acid and dissolved by hydrochloric acid. Gold and platinum do not dissolve in nitric or hydrochloric acid alone, but a mixture of the two acids (aqua regia) at once converts them into the soluble chlorides.

In the same manner as the metals, most of the metallic oxides are insoluble in water, but form with most of the acids soluble salts. It is characteristic of many substances that they are insoluble or difficultly soluble in water and other solvents: barium sulphate, for example, is neither soluble in water nor in dilute acids.

In distinguishing between different bodies it is especially important to notice whether they possess acid or alkaline properties, or whether they belong to the class of salts or other indifferent bodies. Bodies with acid properties which are soluble may often be recognized by their sour taste, but more easily and certainly by their action on certain vegetable colouring matters. The blue solution of litmus or of violets in water is at once turned red by them. Paper which has been dipped in a solution of litmus and then dried has a blue colour and is called litmus paper; when a single drop of an acid solution is allowed to fall on a strip of this paper

the spot is at once coloured red. Bodies which, on the other hand, possess alkaline properties render a solution of litmus, made faintly red with an acid (or red litmus paper), at once blue again, while the solution of violets is turned green. In this sense we speak of an *acid* or *alkaline reaction*.

But besides the soluble bodies with an acid or alkaline reaction a large number of insoluble acids and bases exists which can neither be recognized by their taste nor by their reaction. That certain of these are acid bodies is proved by the fact that they can combine with strong bases to form chemical compounds, from which they can be again separated by stronger acids. Silica, for example, which is insoluble in water and most acids, and which therefore neither tastes sour nor possesses an acid reaction, unites easily with caustic potash to form a compound called water-glass, from which it is again separated by hydrochloric acid. In the same manner, black copper oxide, a body quite insoluble in water, is readily dissolved by nearly all acids, and is again thrown down in the insoluble state by the action of a stronger base, such as caustic soda.

A *salt,* whether soluble or insoluble in water, is the substance produced by the union of a base with an acid. By this process the properties of the acid and base are apparently lost. Most salts possess neither an acid nor an alkaline taste; those which are soluble in water have a peculiar so called saline taste, and generally do not act upon litmus either red or blue. By the union of an acid and a base to form a salt both are said to be *neutralized.*[1]

If we take a little strong solution of caustic potash in a beaker, and add to it strong nitric acid, with constant stirring, the liquid will become strongly heated, and if we at last add the acid carefully drop by drop, we shall ultimately reach a point when the liquid neither possesses an alkaline nor an acid reaction. The liquid is now neutral, and has neither an alkaline nor an acid, but a pure saline taste. It now contains a salt—nitre—which crystallizes out in large prisms on cooling the liquid.

In the same way, if we neutralize caustic soda with sulphuric acid, we obtain Glauber's salt, which also crystallizes out on cooling.

Are, it might be asked, the sulphuric acid and the soda, the nitric acid and the potash destroyed by this process of neutraliza-

[1] For further remarks on the constitution of salts, see sequel.

tion and production of a salt, or is it possible to reproduce the original substances from the respective salts?

This question has been answered by experiment. The reproduction of the original acid and base from an aqueous solution of the salt may be done in various ways; the simplest method is to pass an electric current by platinum electrodes through a saturated aqueous solution of Glauber's salt, coloured violet by a neutral solution of litmus. The salt is then decomposed, and, by interaction with the water, the alkali (soda) appears at the negative pole, while the acid (sulphuric acid) is set free at the positive pole,[1] these bodies being recognized by the blue colour of the solution around the negative pole and the red colour round the positive.

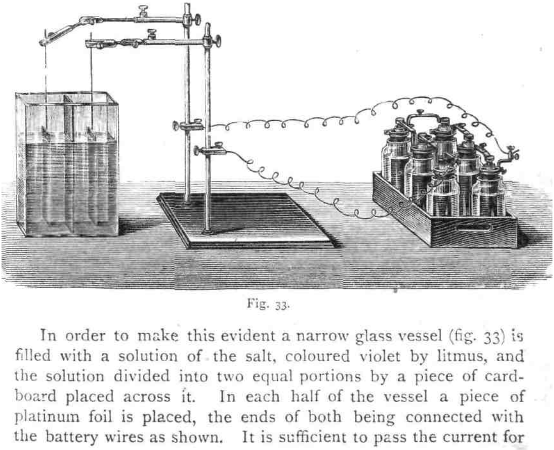

Fig. 33.

In order to make this evident a narrow glass vessel (fig. 33) is filled with a solution of the salt, coloured violet by litmus, and the solution divided into two equal portions by a piece of cardboard placed across it. In each half of the vessel a piece of platinum foil is placed, the ends of both being connected with the battery wires as shown. It is sufficient to pass the current for

[1] The first decomposition of the salt (Na_2SO_4) is into sodium (Na_2) and the radical SO_4; but the sodium at once decomposes the water, liberating hydrogen and forming sodium hydrate (caustic soda): thus, $Na_2 + 2H_2O = 2NaOH + H_2$; these two substances appearing at the negative pole. At the same time the SO_4 radical breaks up into SO_3 and oxygen, the former uniting with water to form sulphuric acid. The substances liberated at the positive pole are therefore sulphuric acid and oxygen.—ED.

a few minutes, in order to clearly perceive that the one half becomes blue and the other red.

By this apparatus it may also be shown that the quantity of acid set free by the current from the salt exactly corresponds with the quantity of the base so liberated; that, in other words, the quantities of the two substances liberated are in the same proportion as they were combined in the original neutral salt. For if, after breaking the current, the cardboard partition is removed and the liquid well mixed, the acid and base again unite with one another, neutrality is restored, both the blue and red colours being changed into the original violet.

WATER.

We have learnt that water is not, as was previously thought, a simple body, incapable of decomposition, but that it consists of oxygen and hydrogen. We have further seen how water may be built up from its constituents, and in a constant proportion by weight or volume, and how it may be again decomposed into them.

As a chemical compound, water is full of interest. It occurs in nature in all three states of aggregation—solid as ice or snow, liquid as ordinary water, and gaseous as water-vapour or steam.

Liquid water is a tasteless, odourless liquid, and is often, but wrongly, thought to be colourless; in thick layers it has a deep-blue colour. This colour may be seen by taking a wide glass tube about six feet long, of which the sides are thoroughly blackened, and one end closed with a plate of glass, and which is filled with chemically pure water. If then the tube is held in a vertical position, and a white porcelain basin viewed through it, the latter will appear beautifully blue. The true colour of water only appears when it is *perfectly* pure: the slightest trace of an organic substance renders the colour a more or less pronounced green or yellow. It is the blue colour of water which causes the walls of the celebrated blue grotto of Naples and everything contained in it to be of a blue colour. The opening to the grotto is almost closed by water, and it therefore receives nearly all its light through the clear, pure water of the sea.

Ice also possesses a colour of its own. It is bluish-green, and may be well seen in the light passing through the walls of grottoes, which are sometimes hewn out of glaciers.

Water becomes solid at 0°, and crystallizes in the hexagonal system, which may be recognized in the irregularly grouped crystals of snow, or in water frozen on the windows in winter. On the passage of water from the liquid to the solid state, its volume does not diminish, but increases. Ice occupies a larger volume than the water from which it is produced, and has, therefore, a lower specific gravity (0·917) than water at 0°, on which it floats. In this respect, water forms an exception to the rule that liquids in becoming solid contract. This peculiarity is shared by a few other bodies, among the metals by bismuth.

This apparently unimportant property of water is of the greatest value in nature. If ice were specifically heavier than water, the rivers and oceans would not become covered with a protecting crust of ice, as is now the case, but as soon as ice was produced it would sink to the bottom, a fresh layer would be formed on the surface, this would again sink, until the whole mass of water were converted into a solid block of ice, which the heat of summer would only very slightly melt. If this were so, it is no exaggeration to say that animal and vegetable life would be impossible on the earth.

Water possesses its greatest density at 4° (point of maximum density); if heated above this temperature, or if cooled below it, water expands. The expansion of water on freezing, although only slight, is the cause of many important phenomena. Rocks, the crevices and cavities of which become filled with water, are broken up and disintegrated by the freezing of this water in the winter. In this way the process is commenced by means of which the hard rocks are converted into friable, fruitful soil. The force of the expanding ice is so powerful that a hollow iron vessel completely filled with water is burst when the water freezes.

Water is a volatile substance, and even evaporates at the ordinary temperature of the air; ice is also volatile, and gives off vapour at temperatures below 0°, without melting. Water boils at 100° and then forms a colourless vapour or gas, commonly called steam. This vapour becomes visible on escaping into the air owing to its partial condensation. The boiling-point of water, like that of all other liquids, depends upon the pressure. It is 100° under the ordinary pressure of the air (760 mm.), and rises to 120° under a pressure of two atmospheres, and higher still when the pressure is still more increased, as in the boilers of high-pressure steam-engines. Under a less pressure than the ordinary atmospheric

pressure—*e.g.* on high mountains, or under the receiver of an air-pump—water boils at a lower temperature than 100°.

Water as it occurs in nature is never chemically pure; it contains varying quantities of mineral and organic substances dissolved or suspended in it. Natural waters may be divided according to their occurrence into: rain-water, spring-water, river-water, mineral waters, and sea-water. The last named contains the greatest quantity of dissolved mineral substances, principally common salt, and in such quantities as to make it quite unfit for drinking purposes.[1] Mineral waters, of which many are used for medicinal purposes, contain very different substances dissolved in them, often in considerable quantities. We distinguish: *saline-waters*, which contain as their chief constituent common salt, or, when bitter, magnesium sulphate (Epsom); *carbonated-waters*, with free carbonic acid and other mineral constituents (Apollinaris, Seltzer); *alkaline-waters*, with considerable quantities of sodium carbonate, &c. (Vichy); *chalybeate-waters*, containing ferrous carbonate, or some other compound of iron (Spa, &c.); *sulphuretted-waters*, with sulphuretted hydrogen gas dissolved in them (Harrogate); *siliceous-waters*, containing silica (geysers of Iceland), &c.

Ordinary spring- and river-waters contain a smaller quantity of mineral constituents than the true mineral waters. The chief substances contained in these waters are common salt, calcium carbonate, calcium sulphate, magnesium carbonate, magnesium sulphate, and free carbonic acid. These substances are derived from the rocks of the district in which the spring occurs or through which the river flows. *Tales sunt aquae qualis terra, per quam fluunt.* If a spring rises, for example, through chalky or limestone rocks, as in Kent, Berkshire, &c., the carbonic acid which the water obtains from the air enables it to dissolve and take up some of the chalk—calcium carbonate. Should the district contain gypsum (calcium sulphate), as in Cheshire, the water will dissolve a portion of this substance. If, again, the neighbouring rocks contain magnesia (*e.g.* the dolomite rocks of Derbyshire), a portion of the magnesium carbonate will pass into solution in the water. Lastly, spring- and river-waters may be nearly pure if the rocks through which they pass are chemically unacted upon by water. For this reason the natural waters in many parts of Wales and Scotland contain remarkably small quantities of solid constituents.

[1] Sea-water contains about 3·6 per cent. of solids.—ED.

Rain-water, the purest of natural waters, contains small quantities of carbonic acid, compounds of ammonia and nitric acid, particles of dust, &c., which it takes up from the air in falling through it.

Ordinary potable waters are roughly divided into two classes: *hard* and *soft*. A hard water requires more soap to produce a good lather, and does not boil vegetables so well as soft water. Hard waters may further be divided into *temporarily hard* and *permanently hard* waters. The former become soft on boiling or on the addition of lime-water; their hardness is due to calcium carbonate, which they contain held in solution by carbonic acid. On boiling, the gas is driven off, and the calcium carbonate (chalk) deposited; this is how the *fur* of kettles and the *scale* of boilers are produced. On the addition of lime-water, the lime combines with the carbonic acid to form calcium carbonate, which is precipitated with that originally present, according to the equation:—

$$\underset{\text{Calcium carbonate}}{CO\cdot O_2Ca} + \underset{\text{Carbonic acid}}{CO_2} + \underset{\text{Calcium hydrate}}{Ca(OH)_2} = \underset{\text{Calcium carbonate}}{2CO\cdot O_2Ca} + \underset{\text{Water}}{H_2O}.$$

Permanently hard waters contain either calcium sulphate (gypsum) or some compound of magnesium. As their name implies, they are not softened by boiling, because the salts which cause their hardness are slightly soluble in water under all conditions.

Well-water, especially in towns, or near dunghills or stables, is often contaminated with nitre and other nitrates, and organic matter, produced from the decomposing animal matter which penetrates through the soil. Such water often appears quite bright and has no unpleasant taste, but if drunk it may be exceedingly injurious to health. Many epidemics of typhoid and other diseases may be traced to the use of water contaminated with decomposed organic substances. The influence of the drinking water of a town on the general health has of late years been more and more generally acknowledged, and hence the importance of supplying all towns with ample quantities of wholesome water.

Chemically pure water is thus unknown in nature. In order to prepare it, ordinary water is converted into steam by heating it, and this again condensed in suitable vessels to liquid water. This process is called distillation, and the water so prepared is *distilled water.*

The simplest apparatus for this purpose is an ordinary glass retort, furnished with a receiver for cooling, also of glass. For the preparation of larger quantities of distilled water the steam is evolved from the top of a metallic boiler, best of tinned copper, and condensed in a tinned tube by cold water. The process of the slow distillation of water goes on largely in nature. Clouds are produced from the aqueous vapour formed by the slow evaporation of the water of rivers and the sea ; and rain falls when this water vapour is still further condensed. Rain-water or melted snow is thus distilled water, and might be used in place of the latter if it were not rendered slightly impure by falling through the air.

In order to determine whether a specimen of water is pure, or at least free from mineral substances, a portion may be evaporated to dryness in a clean silver or platinum dish. Pure distilled water leaves no trace of a solid residue. Should a residue remain which blackens on heating, organic matter is present in the water, although the water may be contaminated with organic substances and the residue not blacken on heating.

Water is the common solvent for a large number of solids—acids, bases, and salts. A solution is said to be *saturated*, when it can take up no more of the substance dissolved in it. The quantity of a substance required to produce saturation depends chiefly on the temperature ; most bodies are more soluble in hot than in cold water, and we therefore distinguish between a hot and a cold saturated solution.

A hot saturated solution of a substance, which is more soluble in hot than cold water, usually deposits the excess on cooling in the solid state—often as crystals.

The hot saturated solutions of some bodies, if allowed to stand quietly while cooling, do not deposit the excess of the salt. But when the cold liquid is touched with a solid body, or when a particle of dust falls into it from the air, crystallization begins at once, and in some cases (*e.g.* sodium sulphate) the quantity of salt separated is so great that the whole mass becomes solid. Such solutions are called *supersaturated* solutions. Even water itself possesses a similar property. When in quite clean vessels, free from grease, it can be cooled several degrees below 0° without solidifying ; but the slightest shaking is then sufficient to immediately convert the whole mass into ice.

Water is also a solvent for many liquids—*e.g.* sulphuric acid,

alcohol, glycerine. But as the solution in these cases is mutual—*i.e.* water dissolves also in these liquids—we say that sulphuric acid and water, or alcohol and water, mix with one another. Sometimes the mixture of the two liquids, as those we have named, takes place in any proportion, but with other liquids only within certain limits. Water and ether mix with one another, but only within certain limiting proportions. If an excess of ether is added it will remain floating on the surface of the water undissolved.

Nearly all gases are more or less soluble in water. Some, as ammonia and hydrochloric acid, dissolve in very large quantities (up to 800 times the volume of the water or more). In these cases a large quantity of heat is set free, owing to the change in aggregation, the gas losing its latent heat on becoming liquid. Other gases only dissolve slightly in water, as carbonic acid, oxygen, &c., while others, again, scarcely dissolve at all—*e.g.* hydrogen, nitrogen. In all cases, when no stable chemical compound has been produced, the dissolved gases may be again driven out by boiling—for example, carbonic acid and ammonia; hydrochloric acid, on the other hand, can be only partially expelled by boiling.

Many substances, particularly salts, which separate out in the crystalline form from aqueous solutions, retain water mostly chemically combined in a loose manner. This water is called *water of crystallization.* Crystallized washing soda and Glauber's salt contain more than 50 per cent. of this water. According to the temperature at which the crystallization takes place, the quantity of water of crystallization taken up by any particular compound may vary, but the weight of the water is to the weight of the substance with which it is combined always in some definite proportion of their molecular weights. In crystallized soda, one molecule of sodium carbonate is combined with ten molecules of water; common alum contains one molecule of potassium-aluminium sulphate united with twelve molecules of water.

Many compounds (*e.g.* soda) contain their water of crystallization so loosely united, that they part with it, or a portion of it on standing in the air. The crystals then lose their lustre and shape, they become dull, opaque, and often fall to pieces, being converted into an amorphous powder. This phenomenon is called *efflorescence.* The reverse of this, or the attraction which many crystalline and other solids have for water, so that if exposed to the air they take up water and ultimately form a liquid, is called *deli-*

quescence. Calcium chloride and magnesium chloride are examples. All salts do not combine with water when they crystallize out from an aqueous solution; common salt, nitre, potassium chlorate and others crystallize without water. We are unacquainted with the cause of this different behaviour.

Those compounds which do not lose their water of crystallization at the ordinary temperature do so at 100° or a slightly higher temperature. Many salts, however, contain a portion, usually one molecule, of their water of crystallization more firmly combined. Blue vitriol (copper sulphate), which crystallizes with five molecules of water, readily gives off four of them at 100° or 120°, but may be heated up to 180° without losing the last, which it only does at a temperature between 180° and 200°. Green vitriol (ferrous sulphate) and other similar salts, which crystallize with seven molecules of water, retain their last molecule in the same firm manner.

This last molecule of water is not really water of crystallization. It may be called *water of constitution*, because it can be displaced by salts. Zinc sulphate crystallizes with seven molecules of water ($SO_2 \cdot O_2Zn + 7H_2O$), but the double salt of zinc sulphate and potassium sulphate, which crystallizes out from a mixed solution of the two salts, does not contain seven but only six molecules of real water of crystallization ($SO_2 \cdot O_2Zn + SO_2 \cdot O_2K_2 + 6H_2O$). The seventh molecule of water in the zinc sulphate has been displaced by potassium sulphate.

If we bring sulphuric anhydride or calcium oxide into contact with water, a large quantity of heat is set free and the substances unite with one another to form compounds from which the water can be only difficultly or not at all expelled by heat. If the product of the union of sulphuric anhydride and water, which has the composition $SO_3 + H_2O$, be heated up to 340°—*i.e.* far over the boiling point of water—the water is not expelled, but the whole compound distils over. But we can again obtain water from it at the ordinary temperature by adding a metallic oxide. In the same manner, water is set free on the addition of an acid to the compound of calcium oxide with water. Such compounds are called *hydrates*, and the water, *water of hydration* (p. 56).

In reality these hydrates do not contain water as such. The compound produced by the union of calcium oxide and water (slaked-lime) is not to be considered as a compound of the two substances, and cannot, therefore, be represented by the formula

CaO,H_2O. It is a calcium salt, which may be compared with calcium nitrate, containing two atoms of hydrogen in the place of the two atoms of the radical NO_2. Thus :—

$$Ca\begin{cases} O\cdot NO_2 \\ O\cdot NO_2 \end{cases} \qquad\qquad Ca\begin{cases} OH \\ OH \end{cases}$$

Calcium nitrate — Calcium hydrate

In the same manner, the acid hydrates (the true acids), for example, sulphuric acid, nitric acid, are not really compounds of water, but salts containing hydrogen instead of a metal :—

$$SO_3 + H_2O = SO_2\begin{cases} OH \\ OH \end{cases}$$

The hydrates may be called *hydrogen salts*, and there are two classes to be distinguished : (i.) those in which the hydrogen takes the place of a metal—the oxy-acids ; (ii.) those in which the hydrogen displaces an acid-radical—the hydrates proper (see, in App., note on p. 56)—as, calcium hydrate, potassium hydrate (KOH), &c.

Many of these compounds are easily decomposed, some even (copper hydrate) under 100°. Others are so unstable that they cannot exist at the ordinary temperature of the air, or under ordinary conditions generally. If a strong base is added to an aqueous solution of a mercuric salt, mercuric oxide and not mercuric hydrate is precipitated ; and from an aqueous solution of a carbonate, a strong acid will liberate carbonic anhydride (commonly called carbonic acid), and not its hydrate or the true acid.

The crystals of many salts, which crystallize without water, often enclose small quantities of water mechanically. On heating these crystals they break into pieces, often with violence, or, as we say, they *decrepitate.*

Water is deposited on solid bodies from the air, and the quantity depends upon the nature of the substance, temperature, relative moisture of the air, &c. In order to remove this moisture, or generally to abstract loosely combined water from bodies which will not bear heating, the substances are placed under a *desiccator*—*i.e.* in a closed space in which the air is kept dry, and the water-vapour which is given off is chemically absorbed. This may be best done by concentrated sulphuric acid. The simplest construction for a desiccator is a bell-jar with ground edge, which is placed on a ground-glass plate over a vessel of sulphuric acid and a separate vessel containing the substance. The air in the bell-jar becomes

quickly dried by the sulphuric acid, and then the moisture, which is evolved from the water into the dry space, is also absorbed.

The process may be much accelerated, if the air in the bell-jar is partially or entirely exhausted. Such an arrangement is shown in fig. 34. The ground-glass plate is cemented to a plate of iron, which is borne by a brass support. A hole is made in the glass,

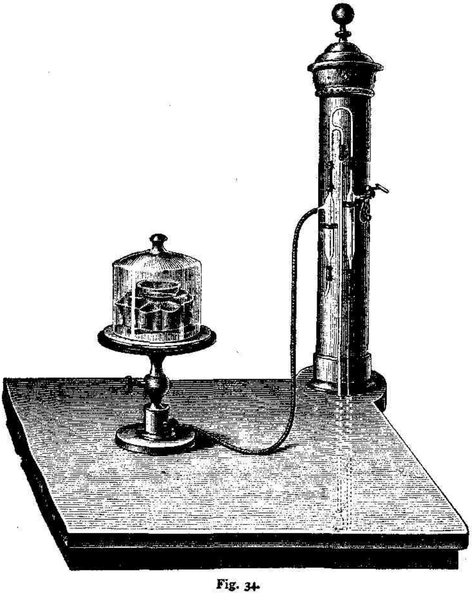

Fig. 34.

and through the iron plate down the brass support to the side tube, above which is a stop-cock. The side tube is connected by a thick piece of india-rubber tubing with a water-air pump, as shown. If now the pump is set in action, the air under the bell-jar soon be-

comes partially exhausted, and, by closing the stop-cock, may be preserved for several days in this condition.

In order to drive off hygroscopic water, or water of crystallization, from those bodies which can be heated without suffering decomposition, an *air-bath* is used. Such an apparatus of the simplest construction is shown in fig. 35. It consists of a copper vessel of which the parts are brazed together and of which the front side opens to form a door. The substance to be dried is placed on a piece of wire gauze, about 6 centimetres from the bottom

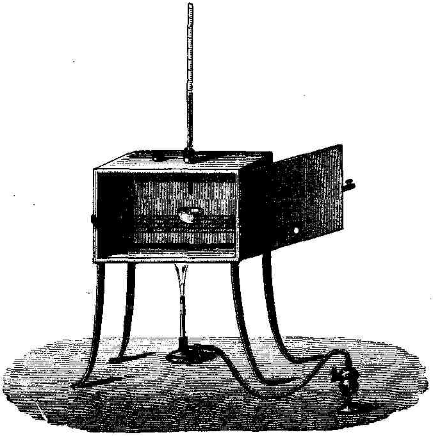

Fig. 35.

of the vessel. After closing the door, the vessel is heated by a gas-lamp, and the flame regulated by the thermometer inserted into the bath from above. In order to get rid of the water-vapour which is thus produced, an opening is made in the top near the thermometer, and a second in one of the side walls just over the bottom. By this arrangement, a slow and continual stream of air flows through the warm bath, carrying with it the water from the substance which is to be dried.

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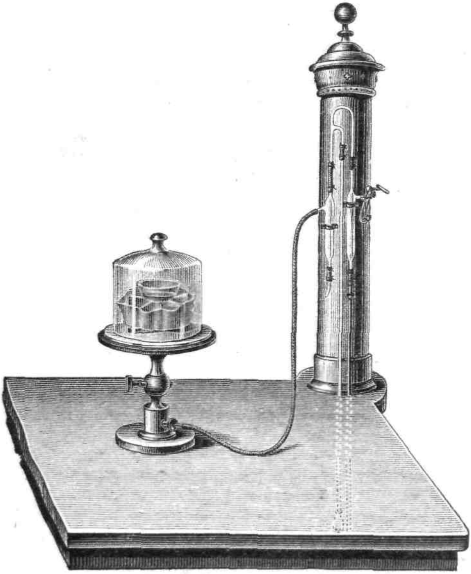

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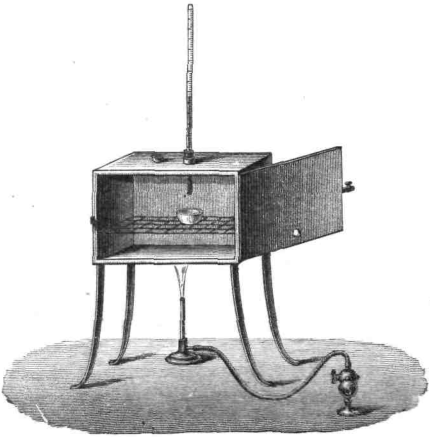

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HYDROGEN PEROXIDE.

Composition : H_2O_2.

Besides water there exists another compound of oxygen and hydrogen which contains twice as much oxygen as water. This compound, called hydrogen peroxide or hydroxyl, was discovered by Thénard in 1818.

It is a colourless, transparent, viscid liquid, with a peculiar odour, mixes with water in every proportion, is not yet known in the solid state, and is very easily decomposed. The pure compound is decomposed even at 15° or 20° into oxygen and water; in an aqueous solution, especially when containing a little hydrochloric acid, it is much more stable.

Hydrogen peroxide cannot be prepared directly from oxygen and hydrogen, but is formed when the oxygen of peroxides combines with hydrogen. Some peroxides (for example, those of manganese or lead) cannot be used for its preparation; it is best to employ barium peroxide, obtained by heating barium oxide in a stream of oxygen.

The barium peroxide, when finely powdered and mixed with dilute hydrochloric acid, decomposes, not like manganese peroxide when so treated to form water and chlorine, but into barium chloride and hydrogen peroxide :—

$$\underset{\text{Barium peroxide}}{BaO_2} + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Barium chloride}}{BaCl_2} + \underset{\text{Hydrogen peroxide}}{H_2O_2}$$

To prepare pure hydroxyl, impure barium peroxide (p. 410) is dissolved in dilute hydrochloric acid. To this is added some barium hydrate to precipitate the impurities. When the precipitate becomes white, the clear liquid is run off and precipitated further with barium hydrate. This gives pure barium perhydrate, from which a pure dilute solution of hydrogen peroxide is obtained by adding it to cooled diluted sulphuric acid. The solution decanted from the barium sulphate is concentrated by evaporation in vacuo. (See App.)

The chemical behaviour of hydrogen peroxide is very remarkable. The readiness with which it decomposes into nascent oxygen and water makes it one of the most powerful oxidizing agents for many substances—*e.g.* for arsenic, sulphurous acid, and many

metallic sulphides. Black lead sulphide is easily converted by it into white lead sulphate. In old oil paintings, in which the light colours produced by white-lead have gradually darkened owing to the formation of lead sulphide, the original colours may be again produced by carefully washing with a dilute solution of hydrogen peroxide. This then converts the lead sulphide into lead sulphate, without damaging the picture.

Hydrogen peroxide acts, however, upon many substances as a reducing agent and abstracts oxygen. If an aqueous solution is added to silver oxide (or manganese peroxide), the liquid froths up and evolves considerable quantities of oxygen. The atom of oxygen which the peroxide contains more than water unites with an atom of oxygen from the silver oxide to form a molecule, and the silver oxide is at the same time reduced to metallic silver :—

$$\underset{\text{Hydrogen peroxide}}{H_2O_2} + \underset{\text{Silver oxide}}{Ag_2O} = \underset{\text{Water}}{H_2O} + \underset{\text{Oxygen}}{O_2} + \underset{\text{Silver}}{Ag_2}.$$

In the same manner manganese peroxide is reduced to manganous oxide, which, when the liquid contains a free acid, unites with it, forming a salt. This remarkable reaction may be used to determine roughly whether a given solution contains much or little hydrogen peroxide. The solution is poured on a little powdered black oxide of manganese contained in a test-tube when a rapid evolution of oxygen at once begins, sufficient to show its presence by kindling a glowing chip of wood.

To detect traces of hydrogen peroxide in an aqueous acid liquid, a little ether is added, and one drop of a solution of potassium bichromate ; after shaking, the ether, as it rises to the surface, is found to be tinged with a beautiful blue colour, due to some compound of chromium containing more oxygen than chromic acid, probably $Cr_2O_7nH_2O$ (see perchromic acid, p. 474). Ozone does not give this colour.

OZONE.

Composition : O_3.

It was long known that on turning the glass plate of an electrical machine a peculiar odour may be noticed, very similar to that produced when phosphorus is allowed to oxidize slowly in moist air. Careful experiments have shown that the cause of this odour is a chemical compound produced by these and other pro-

cesses from the oxygen of the air. To this body the name **ozone** has been given.

Ozone is an allotropic modification of oxygen, and its relation to ordinary oxygen is somewhat the same as that of ordinary phosphorus to the red amorphous modification of this element. In the same manner as ordinary phosphorus has a much more powerful affinity for oxygen, sulphur, and other elements than the red phosphorus, so the affinity of ozone for most substances is very much greater than that of ordinary oxygen. And, again, as common phosphorus is converted into the red variety on heating, so also is ozone converted by heat into ordinary oxygen.

Ozone has never yet been prepared chemically pure, and particularly never free from ordinary oxygen. In all attempts to convert oxygen into ozone, a considerable quantity, always the greater part of the former gas, remains unchanged. Our ideas, therefore, of the properties of ozone refer only to a mixture of it with oxygen.

It is a colourless gas,[1] with a very intense odour, soluble in water, to which it imparts its smell; it acts in an irritating manner when inspired, and attacks the bronchial tubes in the same manner as chlorine. Ozone is condensed to the liquid state more easily than oxygen, and then forms a blue liquid of varying tints according to the pressure.

Ozone occurs in atmospheric air, although only in very minute quantities. The oxygen evolved from plants appears to contain minute traces of ozone. Moreover, during many chemical changes (see below, oxidation of phosphorus) in which atoms of oxygen are set free at a low temperature, some, though always but a very small proportion of the whole, unite to form ozone. Various organic compounds—*e.g.* oil of turpentine, oil of bitter almonds—possess the property, when exposed to the light, of converting the oxygen of the air into ozone, absorbing it mechanically. If water is present, hydrogen peroxide is produced, and not ozone.

The partial conversion of oxygen into ozone may be brought about by allowing electric sparks to pass through the gas, or by allowing phosphorus, half covered with water, to oxidize slowly to phosphorous acid in a large vessel. In the latter case the ozone produced soon combines chemically with the phosphorous acid.

The best method to obtain ozone in comparatively speaking large quantities is to subject a slow stream of oxygen or atmospheric air to the action of high electric potential without allowing

[1] On looking through a tube several yards long and filled with ozonized

sparks to pass through the gas. By this silent discharge of the electricity through the oxygen which then takes place several per cent. of the gas is converted into ozone—a very remarkable fact,

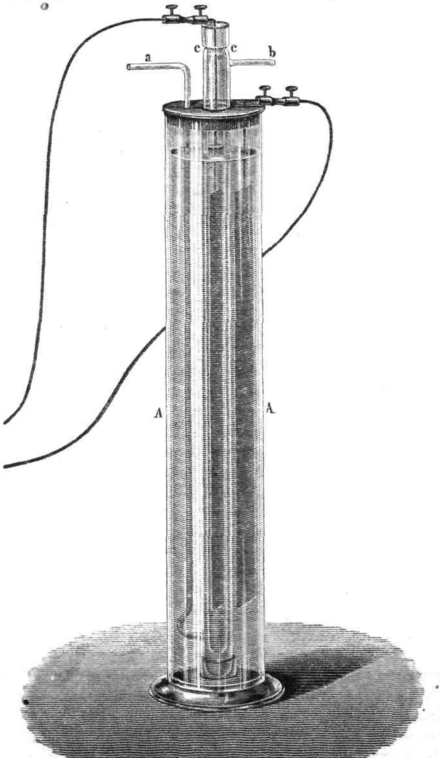


Fig. 26.

and one which suggests the question whether other gases might not also be changed in the same way.

The figure on the preceding page (fig. 35) shows an apparatus which yields large quantities of ozone, and which may be easily made by a skilful glass-blower. Through the centre of the wooden lid of the cylinder A A passes a wide glass tube, open at the top and closed at the bottom. At the lower end of this tube, near the side, a narrow piece of glass tubing is melted, which is bent upwards and again at right angles (*a*) above the lid. By this tube the oxygen enters, and by the tube *b* it leaves the apparatus when partially converted into ozone.

In order to produce this conversion of oxygen into ozone, a second rather smaller tube is placed inside the wide one. This tube is also open at the top and closed at the bottom, and the two tubes are melted together air-tight at the line *c c*, in such a manner that the gas, entering at *a*, passes through the narrow annular space between the two tubes, and finds an exit at *b*. The inner tube and the wide cylinder are filled to about the same height with dilute sulphuric acid (1 of acid to 10 of water); in each of them dips a piece of platinum foil to which is melted a piece of stout platinum wire. Both wires are now attached to a powerful induction coil, and at the same time dry oxygen is allowed to enter at *a*.

The two platinum plates and the sulphuric acid with which they are in contact become strongly electrified, and discharge themselves silently, without the production of sparks, through the space between the two tubes, by means of which the oxygen is partially converted into ozone.

Ozone is one of the most powerful oxidizing agents. It so exceeds ordinary oxygen in this respect that it often oxidizes bodies at the ordinary temperature which only combine with oxygen when heated. The metal mercury, which may be kept for years in the air without any alteration, becomes at once covered with a film of the oxide when exposed to the action of ozone. Silver is also oxidized and converted into the peroxide by ozone. Sulphuretted hydrogen and sulphurous acid are rapidly converted into sulphuric acid, and black lead sulphide, which remains unchanged for years in ordinary oxygen, is at once changed into white lead sulphate.

In the same manner as chlorine, ozone easily expels iodine from its compounds. Iodine, when free but not when combined, possesses the property of colouring starch paste blue, even when

only minute traces of it are present. If, therefore, dilute starch paste is mixed with a solution of potassium iodide and strips of white paper are moistened with the mixture, the paper will become blue when brought into contact with air containing ozone, and the reaction will be all the more rapid the greater the quantity of ozone present.

This very delicate test enables us to find out whether air contains ozone.[1] The reaction is expressed by the equation :—

$2KI$	+	O_3	+	H_2O	=	$2KOH$	+	I_2	+	O_2.
Potassium iodide		*Ozone*		*Water*		*Potassium* hydrate		*Iodine*		*Oxygen*

The powerful oxidizing action of ozone makes it an energetic bleacher, and if it should later happen that ozone could be prepared in such quantities and as easily as chlorine, it would be very generally employed for this purpose. The success of the old process of meadow bleaching possibly depends upon the action of ozone. Litmus and other vegetable colouring matters are completely decolorized by introducing them into ozonized oxygen. Even indigo, which is otherwise a very permanent colour, cannot withstand the action of ozone. It is soon decolorized and converted into a new chemical compound by the action of ozone upon it.

The difference between the molecular composition of ozone and ordinary oxygen has been determined by experiment. It was found that when electric sparks passed through oxygen, or, better, when the gas was subjected to the silent discharge, its volume diminished. The ozone which was produced must therefore be denser than oxygen. Exact experiments yielded the result that by this process three volumes of oxygen were condensed to two volumes of ozone, so that ozone must be one and a half times as dense as oxygen. And it was further observed that when the mixture of ozone and oxygen was again converted into oxygen by heating it regained its original volume.[2]

From these experiments, and from the fact that the molecule of oxygen contains two atoms, it is concluded that the molecule of ozone contains *three* atoms. If this is correct, the powerful oxidizing properties of ozone are explained on the supposition that its molecule breaks up into a molecule and a free atom of oxygen—

[1] This test does not prove conclusively that ozone is present, as other bodies, such as nitrous acid, hydrogen peroxide, also colour the paper blue.—ED.

[2] See Appenc

$O_3 = O_2 + O$ – the latter then exercising the same force of affinity as oxygen in the nascent state—*e.g.* when set free by the electric current.

Ozone, like hydrogen peroxide, is thus a valuable and easily obtained source of nascent oxygen. It may possibly assume very considerable importance in medicine and the arts at no distant date.

THE HALOGENS OR SALT-PRODUCERS.

The four elements chlorine, bromine, iodine, and fluorine are grouped together under this name because they form salts by direct union with the metals (ἅλς, sea-salt, and γεννάω, I produce). These salts are called *haloid-salts* to distinguish them from the *oxy-* and *sulpho-salts.* The haloid-salts consist of two elements, the halogen element and a metal—for example, sodium chloride, NaCl; while the oxy- and sulpho-salts contain at least three elements, a metal and a simple or compound radical united together by oxygen or sulphur—for example, potassium nitrate, $NO_2 \cdot OK$.

It was thought at one time that every acid and every salt must contain oxygen, and it was long imagined that this element was present in the haloid-salts and that chlorine, bromine, &c., were compounds of oxygen. As, however, all attempts to detect oxygen in the halogens, and as salts of the halogens really containing oxygen were discovered later—for example, potassium chlorate ($ClO_2 \cdot OK$)—the halogens are now considered as elements, as long as we are unable to decompose them.

The chemical compounds of the halogens, particularly those of chlorine, bromine, and iodine, are so similar that they are often difficult to distinguish from one another. It is thus all the more remarkable that these three elements should possess such very different physical properties in the free state. Chlorine is a greenish-yellow gas, bromine a dark red-brown liquid, and iodine is a dark grey crystalline solid with metallic lustre.

CHLORINE.

Chemical Symbol: Cl.—*Atomic Weight*: 35·5.

This element does not occur free in nature, but only combined; its chief compound is common salt (sodium chloride), in which it is united with the metal sodium. But although common salt is one of the most widely distributed chemical compounds, chlorine has only been known for about 100 years; it was discovered in 1774 by Scheele, one of the discoverers of oxygen.

Chlorine is a greenish-yellow gas with a powerful and peculiar odour, and owes its name to its colour (χλωρός, greenish-yellow). It possesses a density of 2·45 compared with air as unity. Its molecular weight is, therefore, $2{\cdot}45 \times 28{\cdot}88 = 71$ (p. 51), and its molecule, like that of hydrogen, contains two atoms. At a temperature of $-40°$, or under a pressure of about ten atmospheres at the ordinary temperature, it is condensed to a dark yellow liquid, with a specific gravity of 1·3. It is dissolved by water in larger quantities than oxygen. One volume of water at the ordinary temperature absorbs about 2·5 volumes of the gas, but at 0° a much greater quantity. At the latter temperature it forms a crystalline compound with water, having the composition, $Cl_2 + 10H_2O$.

If chlorine is breathed, even in small quantities, it attacks the organs of respiration, causes inflammation of the bronchial tubes, and so produces a very troublesome cough. In larger quantities it may produce inflammation of the lungs, followed by death. The chemist must therefore exercise caution in experimenting with this substance.

In the ordinary sense of the word, chlorine is not, like hydrogen, a combustible body—*i.e.* if strongly heated in the air it does not burn. But if an atmosphere of hydrogen be substituted for air, chlorine burns freely, and, conversely, a jet of hydrogen burns in chlorine with a pale, livid flame, producing hydrochloric acid. From this we conclude that the affinity of chlorine for hydrogen is much stronger than for oxygen. Chlorine cannot support the combustion of a piece of glowing charcoal or of a chip of wood, as carbon and chlorine never combine directly with one another.

For the preparation of chlorine its hydrogen compound (hydro-

chloric acid) is almost universally employed. In order to set the chlorine free from this compound, it is only necessary to abstract and convert the hydrogen into some non-volatile chemical compound. It will at once be remarked that the strong affinity of hydrogen for oxygen might be employed, and the chlorine obtained according to the equation :—

$$\underset{\text{Hydrochloric acid}}{2HCl} + O = Cl_2 + \underset{\text{Water}}{H_2O}.$$

And, as a matter of fact, considerable quantities of chlorine may be obtained by passing hydrochloric acid gas and air over red-hot pieces of brick (Deacon's process.) (See App.) But by this method the chlorine remains mixed with large quantities of nitrogen, derived from the atmospheric air, and the process, though suitable for technical purposes, is quite unfit for the preparation of the pure gas.

It is better to employ compounds containing oxygen, and particularly those only loosely combined with the element, such as the peroxides. Most of the metallic oxides are so changed by the action of hydrochloric acid that the corresponding chloride and water are produced, thus :—

$$\underset{\text{Manganous oxide}}{MnO} + 2HCl = \underset{\text{Manganous chloride}}{MnCl_2} + H_2O.$$

Some peroxides behave in the same manner—*e.g.* manganese peroxide :—

$$\underset{\text{Manganese peroxide}}{MnO_2} + 4HCl = \underset{\text{Manganese tetrachloride}}{MnCl_4} + 2H_2O.$$

But these metallic perchlorides are very unstable bodies, and are easily decomposed into the lower chloride and chlorine :—

$$\underset{\text{Manganese tetrachloride}}{MnCl_4} = \underset{\text{Manganous chloride}}{MnCl_2} + Cl_2.$$

From these two equations it is seen how chlorine may be prepared from manganese peroxide and hydrochloric acid, and how only one half of the chlorine is set free.

The preparation of chlorine, according to this method, is best carried out by placing a small quantity of the powdered black oxide of manganese in a large glass flask, and then adding commercial hydrochloric acid until the flask is about one-third full. It is not advisable to introduce more than this into the flask, since the mass froths up during the evolution of the chlorine. When the black

oxide has been thoroughly mixed with the hydrochloric acid, it is gently heated over a gas flame. The reaction begins at the ordinary temperature, and only requires a very gentle warmth to continue it. The atmospheric air is then gradually expelled by the heavier chlorine, and finally the gas itself issues from the tube, which passes through the cork in the neck of the flask.

The chlorine so prepared is always mixed with vapours of *hydrochloric acid. In order to separate these vapours*, and, at the same time, to dry the gas or abstract the water-vapour which it contains, it is passed through two wash-bottles, of which the first is

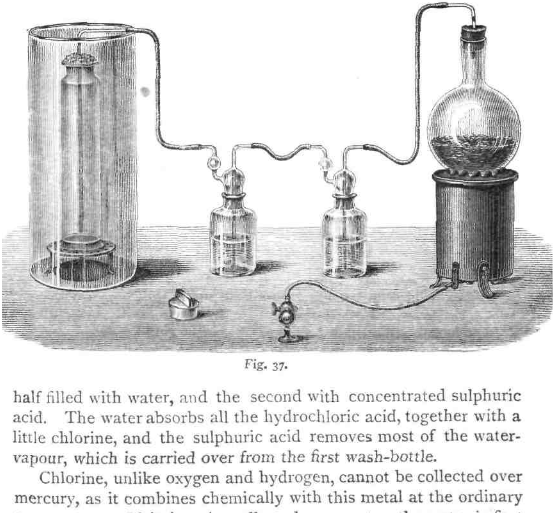


Fig. 37.

half filled with water, and the second with concentrated sulphuric acid. The water absorbs all the hydrochloric acid, together with a little chlorine, and the sulphuric acid removes most of the water-vapour, which is carried over from the first wash-bottle.

Chlorine, unlike oxygen and hydrogen, cannot be collected over mercury, as it combines chemically with this metal at the ordinary temperature. If it is to be collected over water, the water is first made luke-warm, as warm water absorbs much less of the gas than cold. If a vessel is required full of dry chlorine, the tube delivering the gas is led to the bottom of the vessel (fig. 37). The chlorine then gradually displaces the lighter atmospheric air, and the

yellow coloured gas may be readily perceived as it rises in the jar. In order to lessen the communication with the external air, the mouth of the jar is loosely closed with a plug of cotton-wool. The chlorine is led into the jar until the interior appears uniformly coloured, by which time most of the air has been expelled. All such operations with chlorine must be conducted in a good draught of air, on account of the poisonous nature of the gas.

In this method of preparing chlorine, sulphuric acid and common salt may be used instead of the hydrochloric acid. An intimate mixture of one molecular weight of common salt with at least two molecular weights of impure manganese peroxide is prepared, and an excess of dilute sulphuric acid poured over the mixture. In this way all the chlorine is obtained from the common salt, and the end products of the reaction are acid sodium sulphate, manganous sulphate, water, and chlorine :—

$$\underset{\text{Sodium chloride}}{2NaCl} + \underset{\text{Manganese peroxide}}{MnO_2} + \underset{\text{Sulphuric acid}}{3SO_2\left\{\begin{matrix}OH\\OH\end{matrix}\right.} =$$

$$\underset{\text{Manganous sulphate}}{SO_2{\cdot}O_2Mn} + \underset{\text{Acid sodium sulphate}}{2SO_2\left\{\begin{matrix}ONa\\OH\end{matrix}\right.} + Cl_2 + 2H_2O.$$

But the preparation of chlorine from commercial hydrochloric acid and black oxide of manganese is always to be preferred ; it is more rapid and more advantageous, and the bye-product, manganous chloride, may be easily purified.

Chlorine may also be obtained by the electrolysis of a saturated aqueous solution of common salt, or of hydrochloric acid, by employing electrodes of gas-carbon, and placing a bell-jar filled with the same liquid over the positive electrode.

The chemical affinity of chlorine for most of the metals and non-metals is very powerful, and in many cases it even exceeds that of oxygen. The elements, oxygen, fluorine, nitrogen, and carbon, do not, however, combine directly with it, even at the highest temperatures. But compounds of these elements (except fluorine) with chlorine may be prepared in an indirect manner.

The affinity of chlorine for hydrogen is particularly powerful. Equal volumes of the two gases, mixed in darkness or candle-light, unite to form hydrochloric acid when exposed to direct sunlight, or when brought into contact with a burning body or an electric spark. The quantity of heat which is set free on the union of the

two gases and the consequent expansion is so great that even thick vessels are burst with a loud explosion. A mixture of one volume of hydrogen and one volume of chlorine when ignited produces the same effects, and for the same reason, as a mixture of two volumes of hydrogen with one volume of oxygen. A jet of hydrogen, however, when ignited in the air and plunged into a jar of chlorine, continues to burn quietly with a pale flame, also producing hydrochloric acid.

The affinity of chlorine for hydrogen is under some circumstances stronger than that of oxygen for the same element. An aqueous solution of chlorine, exposed to the light, gradually loses its colour; the chlorine expels the oxygen from the water and hydrochloric acid remains behind.

Sulphur unites with chlorine at the ordinary temperature, and more quickly when heated, to form the red volatile liquid, sulphur chloride.

Phosphorus, which at the ordinary temperature neither ignites in air nor in oxygen, catches fire at once in chlorine, forming one of the chlorides of phosphorus.

Antimony, when finely powdered and shaken into a jar of chlorine, burns with light and heat to form antimonic chloride. Copper, in a finely divided state, as Dutch metal, behaves in the same manner, the compound produced being cupric chloride ($CuCl_2$), corresponding to that formed when copper burns in oxygen, cupric oxide (CuO).

Sodium burns in a stream of chlorine, and becomes incrusted with sodium chloride, which is identical in every respect with the naturally occurring common salt.

A lighted taper, the wax or fat of which consists essentially of carbon and hydrogen, when introduced into a jar of chlorine, continues to burn, but only feebly and with a dull red light, large quantities of soot being at the same time liberated. The hydrogen of the wax unites with the chlorine, while the carbon is set free. The same phenomena is shown still more strikingly with volatile hydrocarbons rich in hydrogen—for example, oil of turpentine.

Many organic substances are decomposed by chlorine at the ordinary temperature, and in diffused daylight, the decomposition being often accompanied by a change in colour. If chlorine is led into a blue solution of indigo, or into ordinary black ink, or if chlorine water is added to either of these liquids, they both become yellow owing to the formation of new chemical compounds.

Fresh flowers, and calico coloured with organic colours when moistened with chlorine, lose their colours, or, in other words, they are bleached.

We are acquainted with the new chemical compounds produced by the action of chlorine on indigo and on ink; we know that indigo-blue is converted into yellow isatin chloride, which can be separated and obtained in a crystalline form. But in most other cases, particularly with regard to the unknown colouring matter of flowers, we are as little acquainted with the products of decomposition, when bleached by chlorine, as we are with the chemical nature of the colours themselves.

The action of chlorine in these processes often consists in the abstraction of one or more atoms of hydrogen, which unite with the chlorine to form hydrochloric acid, while a similar number of atoms of chlorine takes the place of the displaced hydrogen. This process of *substitution*, as it is called, often takes place in many colourless organic compounds; the well-known colourless phenol, (carbolic acid), for example, is easily converted by chlorine into monochlorphenol, dichlorphenol, and even trichlorphenol.

In other cases, chlorine acts as an oxidizing agent. We have already seen that chlorine can decompose water in sunlight, forming hydrochloric acid and oxygen; and if at the same time substances capable of easy oxidation are present—and to these belong many organic colouring matters—they become oxidized by the oxygen set free from the water. In most cases, as in the conversion of indigo into isatin chloride, both processes go on together.

The bleaching properties of chlorine make this substance of great practical value. Linen which was previously bleached by exposing it to sunlight on green meadows for weeks together, is bleached by chlorine in as few minutes as the old method required weeks. In the arts, free chlorine is, however, not employed, but a compound called *bleaching powder* or *chloride of lime*, which easily yields up its chlorine, and which is much easier to manage and much less dangerous than the free gas. Books or engravings, which, in course of time, have become stained, may be rendered completely white by placing them for a short time in fresh chlorine water. The printing ink, which consists essentially of carbon (lamp-black), is unacted upon by the chlorine. Characters in ordinary writing ink, which is an organic compound, are at once completely bleached.

In all cases in which chlorine or bleaching powder has been used for bleaching purposes, care must be taken that the chlorine, which adheres mechanically, is afterwards completely removed. Linen, calico, or paper when bleached with chlorine, retains chlorine in the pores so persistently, that it cannot be got rid of by repeated washing with water. Alone this chlorine would have no bad effect, but under the action of light it produces with water hydrochloric acid, which destroys the organic tissues, rendering the fabric so brittle, that it ultimately falls to pieces. The chlorine which is left in the pores of the fabrics, after they have been bleached and thoroughly washed, must be removed by chemical means. For this purpose substances are chosen which are easily oxidized and which themselves exert no injurious action, as calcium sulphite or sodium thiosulphate. The former substance is transformed by chlorine in the presence of water into calcium sulphate (gypsum), the latter into sulphur and sodium sulphate. A substance used for this purpose is called an *antichlor.* Linen bleached in this way is whiter and lasts longer than that bleached by the old method of exposing it to the light and air.

The property which chlorine possesses of decomposing and chemically altering organic and particularly organized bodies gives it another practical application. Chlorine acts as a most powerful disinfectant; it destroys the organic substances which collect in the air of closed spaces, particularly in the chambers of patients suffering from infectious diseases. Experience has shown that the air of sick rooms is purer and healthier when small quantities of chlorine are allowed to evaporate from time to time. This is best done by placing a little chloride of lime in one or more saucers, and moistening it with a little common vinegar. Small quantities of chlorine are then gradually set free.

Chlorine Hydrate: $Cl_2 + 10H_2O$.

Water, which at the ordinary temperature only absorbs a little more than twice its volume of chlorine, takes up large quantities at $0°$, and forms a chemical compound, having the composition shown above. This compound is produced, as small crystalline plates of a yellow colour, by leading chlorine into ice-cold water, until finally the whole liquid becomes semi-solid. The crystals may be filtered off at a temperature below $0°$, and freed from adhering water by pressing between blotting paper. At a few degrees above $0°$ the hydrate is again decomposed into its coustituents. This

property affords an easy method for the preparation of liquid chlorine. The chlorine hydrate is pressed into the end of a thick bent glass tube, which stands in a freezing-mixture, and after a few pieces of calcium chloride have been placed above it, the open end *c* (fig. 38), is fused together by the blow-pipe. If now the limb *c* is placed in a freezing mixture and the other limb *a* gently warmed, the chlorine which is set free condenses in *c* by its own pressure to a yellow liquid, while the water is retained by the calcium chloride.

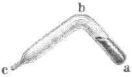


Fig. 38.

HYDROCHLORIC ACID (*Muriatic Acid*).

Composition : HCl.

This substance, the only compound of hydrogen and chlorine, occurs in small quantities in the gases emitted from volcanoes.

It is a colourless gas which fumes strongly in the air, possesses a suffocating odour and taste, and a strong acid reaction. Its specific gravity compared with air as unity is 1·26, and its molecular weight is therefore $1{\cdot}26 \times 28{\cdot}88 = 36{\cdot}39$ (p. 51), corresponding to the formula given it above. Under a pressure of 25 atmospheres and at a temperature of $-4°$ it is condensed to a colourless liquid. Water dissolves large quantities of the gas forming ordinary (aqueous) hydrochloric acid.

Hydrochloric acid is produced by the direct union of chlorine and hydrogen, with a large evolution of heat, when about equal volumes of the gases are mixed and exposed to direct sunlight, or when raised to the temperature of combustion by an electric spark or a flame. If a very thin glass flask (or better, a thin glass bulb) is filled in the dark with a mixture of equal volumes of hydrogen and chlorine, corked firmly, and then exposed to bright sunshine, the moment when the first ray of sunlight strikes the flask or bulb, the union of the two gases at once follows, and the flask is burst by the force of the loud explosion. The combination takes place more slowly in diffused daylight, and is only produced suddenly with an explosion when the two gases are mixed in *exactly* equal proportions in the dark. This mixture of exactly equal volumes may be obtained by the electrolysis of strong aqueous hydrochloric

acid by gas-carbon electrodes, and collecting the mixed gases together after all the air has been expelled from the liquid and the porous carbon, and after the liquid over the positive pole has become perfectly saturated with chlorine.

When one volume of chlorine unites with one volume of hydrogen no condensation occurs, as when oxygen and hydrogen combine together, but two volumes of hydrochloric acid are produced. One volume of the compound gas consists, therefore, of half a volume of chlorine and half a volume of hydrogen. From this it follows that the molecule of hydrochloric acid consists of $\frac{1}{2}$ molecule = 1 atom of chlorine, and $\frac{1}{2}$ molecule = 1 atom of hydrogen ; from this also its density may be calculated, and will be found to agree with experiment, thus :—

1 vol. chlorine	weighs	2·450
1 ,, hydrogen	,,	0·069
2 ,, hydrochloric acid . .	,,	2·519
1 ,, ,, ,, . .	,,	1·26

Again, since 2·519 parts by weight of hydrochloric acid contain 2·45 parts of chlorine and 0·069 part of hydrogen, the percentage composition of the gas, according to the usual simple process, is :—

Hydrogen	= 2·74	parts by weight.
Chlorine	= 97·26	,,
Hydrochloric acid . . .	= 100·00	,,

In other words, this small quantity of hydrogen suffices to completely change the properties of more than 35 times as much chlorine on chemical union with it.

That hydrochloric acid consists of hydrogen and chlorine in equal volumes may be proved by its electrolytic decomposition. A piece of apparatus by which this experiment may be performed is shown in fig. 39. Two glass tubes of equal calibre, which are closed at the top by stop-cocks, are placed in a vertical position, and communicate by a side-tube with a third vertical tube, somewhat longer, and enlarged at the upper end into a bulb. In the lower ends of the two tubes are two cylinders of gas-carbon, which are fitted in water-tight by caoutchouc stoppers, and which are placed in connexion with the two poles of a galvanic battery. The tubes are filled with strong aqueous hydrochloric acid (or a mixture

of hydrochloric acid and a strong solution of common salt) through the bulb-tube, the stop-cocks being open. On commencing the experiment, and for some time afterwards, the stop-cocks are left open, so that the liquid in the tube where the chlorine is liberated may become saturated ; the chlorine which is evolved being carried away by a downward draught as shown in the diagram. If finally

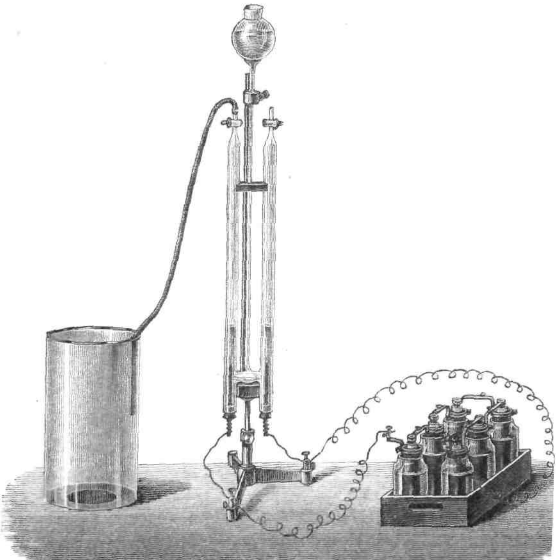


Fig. 39.

the two stop-cocks are closed at the same time, hydrogen collects in one tube and chlorine in the other in equal volumes, and the liquid remains during the experiment at equal heights in the two tubes. The liquid which is displaced by the gases rises in the third tube and collects in the bulb. We see, therefore, from this

experiment that hydrochloric acid contains chlorine and hydrogen in equal volumes.

For the ordinary preparation of hydrochloric acid gas, common salt is almost exclusively used. This salt (sodium chloride), when mixed with concentrated sulphuric acid, gives a large quantity of the gas at the ordinary temperature without heating, and is converted into acid sodium sulphate :—

$$\underset{\text{Sodium chloride}}{NaCl} + \underset{\text{Sulphuric acid}}{SO_2\begin{cases}OH\\OH\end{cases}} = HCl + \underset{\text{Acid sodium sulphate}}{SO_2\begin{cases}OH\\ONa\end{cases}}$$

But if the ordinary crystallized salt, which offers a large surface to the acid, is employed, the mixture always froths over. It is therefore better to use salt which has previously been melted and afterwards broken into moderately large pieces. This evolves the gas more slowly, as its surface is much smaller. The action commences at the ordinary temperature, but must afterwards be supported by a gentle heat.

If rock-salt is used for the preparation of hydrochloric acid, the sulphuric acid must be mixed beforehand with an equal volume of water, and, to free the gas from aqueous vapour, it must be passed through wash bottles containing concentrated sulphuric acid.

Aqueous Hydrochloric Acid.

In the ordinary language of the laboratory, hydrochloric acid means the solution of the gas in water. This is produced by passing a stream of the gas through vessels containing water, which must be kept cold as long as absorption is going on. One volume of water at 0° can absorb about 500 volumes of hydrochloric acid gas, at 20° a less quantity, but still over 400 volumes. During this absorption a considerable quantity of heat is set free, partly in consequence of the chemical attraction between the gas and the water, and partly because of the change from the gaseous to the liquid state. It is therefore necessary to keep the water cool, especially if a cold saturated solution of the gas is required.

This solution of the gas in water (ordinary hydrochloric acid) fumes in the air and possesses the odour of the gas. It reacts and tastes acid even when very largely diluted with water.

A completely saturated solution of hydrochloric acid at 0° has a specific gravity of 1·21. On heating such a solution considerable

quantities of the gas are evolved, and the specific gravity diminishes. When the specific gravity has become 1·145 the liquid boils at 100°. Even at this temperature more hydrochloric acid distils over than water; but on continued boiling the relative quantity of the water passing over with the acid gradually increases, until the boiling point reaches 110°, when it remains constant. The liquid which distils over at this temperature, and 760 mm. pressure, has a constant composition, and a constant specific gravity of 1·1.

This acid, which distils over at a constant temperature and which has a constant composition, does not fume in the air. It contains about 20 per cent. by weight of the gas. It is not, however, a true chemical compound, as its composition is altered if the *pressure* at which it is made to boil is changed. The saturated solution at 0° contains about 42 per cent. by weight of the gas.

Impure aqueous hydrochloric acid is obtained in large quantities as a bye-product in alkali works, in that part of the process in which sodium chloride is converted into sodium sulphate by the action of sulphuric acid. The hydrochloric acid gas, which is given off in immense quantities, is led into large earthenware jars half filled with water, which communicate with one another, so that the gas unabsorbed in the first is absorbed in the second, and so on.

The commercial hydrochloric acid so obtained fumes in the air and has generally a specific gravity of about 1·16, which corresponds to about 33 per cent. of hydrochloric acid by weight. It is generally coloured yellow owing to the presence of iron (ferric chloride) or organic substances, and contains besides small quantities of sodium chloride and sulphate, and always arsenious chloride if the sulphuric acid employed for its production contained arsenic. The presence of this substance may be recognized by the yellow precipitate of arsenious sulphide, produced when sulphuretted hydrogen is added to the acid.

The commercial acid, free from arsenic, may be employed for the preparation of chlorine, and in all cases when the quite pure acid is not required. It may also be employed for the preparation of the pure non-fuming acid of specific gravity 1·1, by distilling in a glass retort until the boiling-point has become constant at 110° and then collecting the distillate. At least one-fourth of the whole must be left behind in the retort to retain all the impurities.

Hydrochloric acid is one of the strong inorganic acids, and

expels many other acids from their salts. With the metallic oxides it forms metallic chlorides and water—*e.g.*

$$\underset{\text{Cupric oxide}}{CuO} + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Cupric chloride}}{CuCl_2} + \underset{\text{Water}}{H_2O}.$$

In the same manner it decomposes many metallic sulphides—*e.g.* ferrous sulphide, antimonious sulphide—liberating sulphuretted hydrogen. It also serves as a solvent for metals. Tin, which is oxidized but not dissolved in nitric acid, easily dissolves in hydrochloric acid, forming stannous chloride and hydrogen :—

$$Sn + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Stannous chloride}}{SnCl_2} + H_2.$$

With most of the peroxides it produces chlorine—*e.g.* manganese peroxide, lead peroxide.

The presence of hydrochloric acid or of a soluble chloride in a liquid may be recognized by the white precipitate of silver chloride produced when silver nitrate is added to the solution. The precipitate is easily dissolved by ammonia and turns black in the light. All chlorides yield chlorine when heated with manganese peroxide and sulphuric acid, and the free chlorine may be easily recognized by its odour and by its bleaching properties.

OXIDES AND OXY-ACIDS OF CHLORINE.

The chemical affinity of chlorine for oxygen is so slight that the two elements cannot be made to unite directly with one another. But compounds of chlorine and oxygen are produced when the one element is brought into contact with the other in the nascent state, or by other indirect means.

We have seen that chlorine and hydrogen unite together only in one definite proportion, but chlorine and oxygen form compounds in five different proportions, of which some are only known as oxygen compounds, others as oxy-acids, or in combination with bases as salts. With the exception of perchloric acid, these compounds are very unstable, and easily decompose into their constituent elements, often with an explosion.

We distinguish the following compounds of chlorine and oxygen, in which the chlorine atom may have a valency from one to seven :—

Oxides.		*Oxy-acids.*	
Hypochlorous anhydride .	Cl_2O	Hypochlorous acid .	$ClO \cdot H$
Chlorous anhydride .	Cl_2O_3	Chlorous acid .	$ClO \cdot OH$
Chlorine peroxide .	ClO_2		
		Chloric acid .	$ClO_2 \cdot OH$
		Perchloric acid	$ClO_3 \cdot OH$

CHLORIC ACID.

Composition : $ClO_2 \cdot OH$.

We may well commence our description of the compounds of chlorine and oxygen with the most important of them—chloric acid. The anhydride corresponding to this acid is unknown, and the acid itself is only known in an aqueous solution. In order to prepare it a solution of potassium chlorate is mixed with fluosilicic acid. The insoluble potassium fluosilicate is filtered off and the acid liquid neutralized with baryta water ; this solution, when filtered and evaporated, deposits crystals of barium chlorate. An aqueous solution of this salt is made and dilute sulphuric acid carefully added, towards the last drop by drop, as long as a precipitate of barium sulphate is produced. The acid liquid, containing the chloric acid, is then filtered off and evaporated in a vacuum over sulphuric acid ; it must not be heated, as it begins to decompose at temperatures over 40°.

So prepared, it forms a thick acid liquid which has not yet been obtained in a crystalline form.

The salts of the acid—the chlorates—are, however, more stable, and of these the potassium salt is the best known and most important. They are obtained when chlorine and nascent oxygen are brought into contact with an alkali, under certain conditions.

Potassium chlorate—$ClO_2 . OK$—is produced in considerable quantities when chlorine is led into a *hot concentrated* solution of caustic potash.[1] The substances produced are potassium chlorate, potassium chloride, and water, of which the potassium chlorate

[1] The delivery tube must be wide or it will become choked by the potassium chlorate.

crystallizes out first on evaporation owing to its being less soluble in water than potassium chloride. The following equation shows the reaction :—

$$\underset{\text{Potassium hydrate}}{6KOH} + 3Cl_2 = \underset{\text{Potassium chlorate}}{ClO_2 \cdot OK} + \underset{\text{Potassium chloride}}{5KCl} + 3H_2O.$$

It is probable that potassium hypochlorite is first produced with potassium chloride, and that the former then breaks up into potassium chlorate and potassium chloride :—

$$\underset{\text{Potassium hydrate}}{2KOH} + Cl_2 = \underset{\text{Potassium hypochlorite}}{ClOK} + \underset{\text{Potassium chloride}}{KCl} + H_2O.$$

$$\underset{\text{Potassium hypochlorite}}{3ClOK} = \underset{\text{Potassium chlorate}}{ClO_2 \cdot OK} + \underset{\text{Potassium chloride}}{2KCl}.$$

Potassium chlorate so prepared always contains more or less potassium chloride mixed with it, from which it may be easily and completely separated by repeated crystallization. The presence of potassium chloride mixed with the chlorate may be easily recognized by the white precipitate of silver chloride produced when a few drops of silver nitrate are added to a solution of the salt, silver chlorate being soluble in water. (See Appendix, note on p. 111 (i).)

Potassium chlorate crystallizes in thin iridescent plates, without water of crystallization. The salt may also be prepared by the direct oxidation of potassium chloride. If a concentrated solution of potassium chloride is electrolyzed by a powerful current, using platinum electrodes, the nascent oxygen which is set free at the positive pole oxidizes the potassium chloride to potassium chlorate.

We have already stated that potassium chlorate is largely employed for the preparation of oxygen (p. 12). The chlorine and oxygen are so feebly held together that the latter gas is completely given off on heating, and potassium chloride remains behind :—

$$\underset{\text{Potassium chlorate}}{2ClO_2 \cdot OK} = \underset{\text{Potassium chloride}}{2KCl} + 3O_2.$$

In the first stage potassium perchlorate is produced, and in such quantities that the method is used for the preparation of this salt. (See Appendix, note on p. 111 (ii)) :—

$$\underset{\text{Potassium chlorate}}{2ClO_2 \cdot OK} = \underset{\text{Potassium perchlorate}}{ClO_3 \cdot OK} + \underset{\text{Potassium chloride}}{KCl} + O_2.$$

On heating more strongly this salt is also decomposed into potassium chloride and oxygen.

In consequence of the slight affinity of chlorine for oxygen the chloric acid of potassium chlorate and other chlorates acts as a powerful oxidizer, something in the same manner as the nitric acid of the nitrates. A red-hot piece of charcoal, on which a little powdered potassium chlorate is sprinkled, burns brilliantly by combining with the oxygen of the salt. A mixture of dried flowers of sulphur and powdered potassium chlorate not only explodes when heated, but also by percussion or even by the heat produced when it is rubbed in a mortar. Caution must, therefore, be exercised in experimenting with this mixture, especially when charcoal powder has been added. A gunpowder containing potassium chlorate instead of nitre—that is, a mixture of charcoal, potassium chlorate, and sulphur—is so explosive that fire-arms charged with it are burst, and potassium chlorate is, therefore, not employed for the manufacture of such explosive mixtures.

Chloric and hydrochloric acids mutually decompose one another, even in dilute aqueous solutions. A portion of the oxygen of the chloric acid oxidizes the hydrogen of the hydrochloric acid, and chlorine together with chloric peroxide are given off.[1] The process goes on when aqueous hydrochloric acid is added to a solution of potassium chlorate :—

$$\underset{\text{Potassium chlorate}}{2ClO_2 \cdot OK} + \underset{\text{Hydrochloric acid}}{4HCl} = \underset{\text{Chloric peroxide}}{2ClO_2} + Cl_2 + \underset{\text{Potassium chloride}}{2KCl} + 2H_2O.$$

Concentrated sulphuric acid acts very energetically on potassium chlorate. The chloric acid which is first produced at once breaks up into oxygen, and the reddish-brown gas chlorine peroxide, which on heating decomposes further into chlorine and oxygen with an explosion.

Chloric acid is a monobasic acid, and all its salts are soluble in water. They may be easily recognized by their oxidizing properties and by the production of chloric peroxide when heated with concentrated sulphuric acid.

[1] This mixture of gases was called *euchlorine* by Davy.—ED.

PERCHLORIC ACID.

Composition: $ClO_3 \cdot OH$.

This compound is a colourless oily liquid of specific gravity 1·78, which does not become solid at $-34°$, fumes in the air, and becomes heated when mixed with water. It is prepared by distilling potassium perchlorate with a large excess of sulphuric acid.

Potassium perchlorate, as we have just mentioned (p. 111), is obtained on heating potassium chlorate. The heating is stopped after the molten salt has ceased frothing and has become viscid or nearly semi-solid. At this point most of the potassium chlorate has been converted into potassium chloride and perchlorate, and as the latter salt is even more difficultly soluble in water than potassium chlorate, it may be easily purified by dissolving in hot water and allowing the solution to crystallize. The salt requires seventy times its weight of water at the ordinary temperature to dissolve it, and separates out from its solution in rhombic prisms.

On heating pure potassium perchlorate in a retort with about four times its weight of concentrated sulphuric acid, perchloric acid distils over as an oily liquid, usually with a yellow colour. When mixed with a small quantity of water it becomes heated and gives a hydrate of the composition $ClO_3 \cdot OH + H_2O$, crystallizing in fine needles. If this hydrate is heated to 110° it decomposes into perchloric acid and a hydrate with the composition $ClO_3 \cdot OH + 2H_2O$, which remains behind in the retort as an oily liquid, boiling only at 203°.

From these facts it will be seen that, although perchloric acid contains more oxygen than chloric acid, it is a much more stable compound. This is also shown in its behaviour when treated with hydrochloric acid. A mixture of potassium perchlorate (or perchloric acid) and hydrochloric acid remains unchanged, while one of potassium chlorate and the same acid evolves chlorine and chloric peroxide. In this way it may be readily seen whether crystalline potassium perchlorate is contaminated with potassium chlorate. Even when only very small quantities of the latter salt are present, the hydrochloric acid becomes yellow and gives off the odour of chlorine.

Potassium perchlorate when heated breaks up into potassium chloride and oxygen, but requires a higher temperature than that necessary to decompose potassium chlorate into potassium perchlorate and oxygen. It deflagrates when thrown on red-hot charcoal in the same manner and for the same reason as potassium chlorate.

The free acid attacks many organic bodies most energetically; it oxidizes them, often with an explosion.

Perchloric acid is a monobasic acid, and all its salts are soluble in water.

CHLORINE PEROXIDE.

Composition: ClO_2.

This body is only known as an oxide and does not combine with water or with bases.

Chlorine peroxide is a most dangerous substance to experiment with, as it easily decomposes with a powerful explosion into its constituents. It is produced, together with perchloric acid, when small pieces of fused potassium chlorate are treated with pure concentrated sulphuric acid and the mixture heated not higher than 40° on a water-bath. It is then evolved as a dark yellow or reddish-brown gas, with a powerful odour, and which often explodes even at this temperature. In a freezing mixture the gas condenses to a red liquid, which boils at about 9°.

CHLOROUS ANHYDRIDE.

Composition: (?) Cl_2O_3.

(See Appendix.)

CHLOROUS ACID.

Composition: $ClO{\cdot}OH$.

Chlorous anhydride is a yellow gas, with an odour similar to that of chlorine. It has a specific gravity of 4·07. Like chlorine, it attacks the organs of respiration, and bleaches even

more powerfully than the element itself. Water dissolves about ten times its own volume of the gas, becoming of a yellow colour. This solution contains chlorous acid—$ClO \cdot OH$, which has, however, never been prepared pure. It bleaches like the gas and produces yellow spots on the skin.

Chlorous anhydride may be easily prepared by abstracting oxygen from a dilute aqueous solution of chloric acid. Nitric acid may be best used to set the chloric acid free from potassium chlorate and arsenious anhydride for the reduction. The following equations show the reactions :—

$$\text{(i.)}\quad \underset{\text{Potassium chlorate}}{ClO_2 \cdot OK} + \underset{\text{Nitric acid}}{NO_2 \cdot OH} = \underset{\text{Chloric acid}}{ClO_2 \cdot OH} + \underset{\text{Potassium nitrate}}{NO_2 \cdot OK}.$$

$$\text{(ii.)}\quad \underset{\text{Chloric acid}}{2ClO_2 \cdot OH} + \underset{\text{Arsenious anhydride}}{As_2O_3} = \underset{\text{Chlorous anhydride}}{Cl_2O_3} + H_2O + \underset{\text{Arsenic anhydride}}{As_2O_5}.$$

For the preparation of the gas 3 parts of arsenious anhydride and 12 parts of potassium chlorate, both in the state of a fine powder, are mixed, and then 18 parts of pure nitric acid of specific gravity 1·33 and 24 parts of water are added. On gently warming the liquid it becomes coloured yellow, and chlorous anhydride is evolved in considerable quantities. The gas may be dried by passing it over calcium chloride, and may then be collected by displacement. At $-18°$ it is condensed to a reddish-brown mobile liquid, which boils a few degrees above $0°$.

Chlorous anhydride is a very unstable compound. At a little above $50°$ it decomposes with explosion into its constituents. Great care must therefore be taken in its preparation, and only small quantities should be prepared at once.

Its aqueous solution combines slowly with bases to form salts—the chlorites—which are mostly soluble in water, and which are easily decomposed on evaporation into a mixture of chlorate and chloride. The lead salt, obtained by mixing a solution of potassium chlorite with lead acetate, is deposited as yellow scales. The general formula of the chlorites is $ClO \cdot OM'$, and the acid is therefore monobasic.

HYPOCHLOROUS ANHYDRIDE.

Composition : Cl_2O.

This compound is a yellow gas with an odour similar to that of chlorine. It has a specific gravity of 2·97, and condenses at $-20°$ to a bright red liquid, boiling at about $+20°$. When heated it is easily decomposed into its constituents, usually with a violent explosion; the liquid decomposes even when shaken. In its preparation great care must therefore be exercised.

The gas is prepared by treating mercuric oxide with chlorine, when the reaction goes on as shown in the equation :—

$$\underset{\text{Mercuric oxide}}{2HgO} + 2Cl_2 = \underset{\text{Mercuric oxychloride}}{HgO,HgCl_2} + \underset{\text{Hypochlorous anhydride}}{Cl_2O}.$$

The ordinary red oxide of mercury, which has been obtained by heating the metal in the air, cannot be employed for the reaction, but the yellow oxide, which has been prepared by precipitating mercuric chloride with caustic soda, and has been carefully washed and dried for some time at 300°, must be used. If dry and pure chlorine is slowly led over such mercuric oxide contained in a long well-cooled tube, it is absorbed and the hypochlorous anhydride gas set free. The gas is easily soluble in water, one volume taking up about 200 volumes of the gas. This solution may be considered to contain

HYPOCHLOROUS ACID—(ClOH),

which has, however, never been prepared in the pure state. A similar aqueous solution of hypochlorous acid may be also easily prepared by shaking up precipitated mercuric oxide with chlorine water. The yellow colour of the solution quickly disappears, and the mercuric oxychloride which is formed at the same time may be separated by filtration. The salts of this monobasic acid—the *hypochlorites*—are also unknown in the pure state, but mixed with other bodies they form important substances in the arts and manufactures.

Bleaching powder, which is manufactured in large quantities and chiefly used for bleaching purposes, yields a mixed solution of calcium chloride and calcium hypochlorite when dissolved in water. This bleaching powder, or chloride of lime (not calcium chloride)

as it is sometimes called, may be considered as a peculiar compound of calcium, oxygen, and chlorine, having the composition (CaOCl)Cl or $Ca\left\{\begin{matrix}Cl\\OCl\end{matrix}\right.$. It is prepared by passing dry chlorine over dry slaked lime (calcium hydrate). When no more chlorine is absorbed, a white powder, which smells faintly like hypochlorous acid, remains behind, having the above composition. This compound, when treated with water, is decomposed into calcium hypochlorite and calcium chloride, according to the equation :—

$$\underset{\text{Bleaching powder}}{2(CaOCl)Cl} = \underset{\text{Calcium hypochlorite}}{(ClO)_2Ca} + \underset{\text{Calcium chloride}}{CaCl_2}.$$

But from this mixture pure calcium hypochlorite cannot be separated. The weakest acids, even carbonic acid, separate the hypochlorous acid from this and all other hypochlorites, and the free acid then readily breaks up into chlorine and oxygen. On this depends the bleaching and oxidizing action of bleaching powder. The articles to be bleached are first dipped in a dilute solution of the powder in water, and then submitted to the action of a dilute acid. The effect produced is the same as if the articles were dipped in chlorine water. The reaction takes place according to the two equations :—

$$\underset{\text{Calcium hypochlorite}}{(ClO)_2Ca} + 2HCl = \underset{\text{Calcium chloride}}{CaCl_2} + \underset{\text{Hypochlorous acid}}{2ClOH}.$$

$$\underset{\text{Hypochlorous acid}}{2ClOH} + 2HCl = 2H_2O + 2Cl_2.$$

For a similar reason bleaching powder is well adapted to disinfect sick chambers. If a little of the powder placed in a saucer is moistened with vinegar (dilute acetic acid), it slowly gives off chlorine (p. 103).

If bleaching powder is digested with water at the ordinary temperature and filtered, the alkaline liquid contains, as we have seen, calcium hypochlorite together with calcium chloride and unchanged hydrate. On boiling this liquid the calcium hypochlorite is decomposed into chlorate and chloride :—

$$\underset{\text{Calcium hypochlorite}}{3(ClO)_2Ca} = \underset{\text{Calcium chlorate}}{\left.\begin{matrix}ClO_2\cdot O\\ClO_2\cdot O\end{matrix}\right\}Ca} + \underset{\text{Calcium chloride}}{2CaCl_2}.$$

If chlorine gas is led into a dilute solution of potassium or sodium

hydrate in the cold, a mixture of the corresponding hypochlorite and chloride is obtained :—

$$2KOH + Cl_2 = KOCl + KCl + H_2O.$$

Instead of the caustic alkalies, their carbonates may also be used. No evolution of carbonic acid is noticed at first, owing to the formation of an acid carbonate. As soon, however, as the chlorine begins to act upon this acid carbonate, carbonic acid is given off. These liquids, which are sometimes called *Eaux de Javelle*, also bleach powerfully on the addition of a dilute acid.

Hypochlorous acid is a powerful oxidizing agent. A solution of bleaching powder or of sodium hypochlorite when added to a solution of manganous sulphate produces first a white precipitate of manganous hypochlorite and hydrate, which rapidly becomes oxidized to the brown manganese peroxide. Similarly, with a solution of lead nitrate lead peroxide is formed.

BROMINE.

Chemical Symbol: Br.—*Atomic Weight*: 80.

This element, which was discovered by Balard in 1826, occurs in nature combined with sodium and other metals and usually associated with sodium chloride. Sea-water and many mineral springs contain small quantities of the compounds of bromine with sodium and magnesium. In the mineral kingdom it occurs, particularly in South America, as silver bromide, and has lately been found combined with potassium in the enormous salt deposits of Stassfurt and other places in Northern Germany. The bromine which is now brought into trade at a low price is chiefly prepared from this last-named source.

Bromine is a dark red-brown liquid, which is nearly opaque even in thin layers, and which possesses a specific gravity of 3·18. It freezes to a crystalline solid, with a metallic lustre, at $-7^{\circ}\cdot3$, and boils at 63°, forming a dark-brown gas. At the ordinary temperature it vaporizes rapidly, so that if a few drops are placed in a large empty flask, the whole soon becomes filled with the brown vapour. Its vapour density is 5·5, according to which it is more than twice as heavy as chlorine and 80 times as heavy as hydrogen.

Its molecular weight is therefore $5{\cdot}5 \times 28{\cdot}88 = 159$, and its molecule, like that of hydrogen, contains two atoms. Bromine, like chlorine, dissolves in water, though in rather less quantity; the solution—*bromine water*—has a brownish colour. In the cold below 4° bromine combines chemically with water to form *bromine hydrate*: $Br_2 + 10H_2O$, which is decomposed at 15°, or is rather more stable than the corresponding chlorine compound.

Bromine has an odour resembling that of chlorine, but more intense (whence its name from βρῶμος = a stink). It attacks the eyes and the mucous membrane of the respiratory organs even more powerfully than chlorine, and great caution must therefore be exercised in performing experiments with it. A single drop allowed to fall on the skin produces a painful, slowly-healing wound.

Bromine may be prepared in the same manner as chlorine by decomposing hydrobromic acid with manganese peroxide. But as hydrobromic acid cannot be so readily obtained as the commercial hydrochloric acid, and is much more difficult to prepare, a mixture of potassium or sodium bromide with manganese peroxide and moderately dilute sulphuric acid answers the purpose better. The hydrobromic acid which is at first produced is at once oxidized to bromine and water by the manganese peroxide. The distillation is best carried out in a tubulated retort fitting air-tight in a receiver, the uncondensed bromine vapour being led away by a good draught. The reaction is precisely the same as in the preparation of chlorine, substituting bromine for chlorine:—

$$2KBr + MnO_2 + 3SO_2\begin{cases}OH\\OH\end{cases} =$$

$$2SO_2\begin{cases}OH\\OK\end{cases} + SO_2{\cdot}O_2Mn + 2H_2O + Br_2.$$

The bromine may be purified by shaking with water, and may be again freed from this substance by calcium chloride or concentrated sulphuric acid.

The extraction of bromine on the large scale is carried out in just the same manner. For this purpose the mother-liquors of the mineral- or sea-waters are employed from which most of the less soluble chlorides have crystallized out. But as these mother-liquors always contain some chlorides, and as the bromides are more easily decomposed by sulphuric acid than the chlorides, only enough sulphuric acid and manganese peroxide are added to the mixture to decompose the bromides. In this way only bromine is obtained. The liberation of chlorine is to be avoided, as it com-

bines with the bromine to form a chloride, which is difficult to separate from the bromine. Small quantities of chlorine may be removed from bromine by distilling with potassium bromide, thus :—

$$\underset{\text{Bromine chloride}}{BrCl_3} + \underset{\text{Potassium bromide}}{3KBr} = \underset{\text{Potassium chloride}}{3KCl} + 2Br_2.$$

In its chemical behaviour, bromine is very closely related to chlorine. The differences in their chemical action may almost all be ascribed to the weaker affinity of bromine in comparison with that of chlorine. This difference may be well illustrated in their behaviour with regard to hydrogen. Although the affinity of bromine for hydrogen is very great, and although a mixture of bromine and hydrogen may be made to combine by heating, the union of the two substances cannot be produced by the rays of the sun, not even the direct rays.

The weaker affinity of bromine is also shown by the fact that chlorine can expel bromine from most of its compounds. The non-metals and metals which burn in chlorine combine under similar circumstances with bromine also. Its affinity for oxygen and carbon is more weak than that of chlorine for these elements. Of the bromides, or the compounds so produced, most are soluble in water ; lead bromide is difficultly soluble, silver bromide quite insoluble.

HYDROBROMIC ACID.

Composition: HBr.

This compound, like hydrochloric acid, is a colourless gas fuming in the air, with a strong acid taste and odour, and very soluble in water. Its specific gravity is 2·71, corresponding to the molecular weight: 81. The aqueous solution agrees also in its leading properties with aqueous hydrochloric acid ; when completely saturated it fumes in the air, and gives off a portion of its hydrobromic acid gas on heating.

As previously mentioned, although sunlight cannot cause the chemical union of bromine gas and hydrogen, they may be made to unite by heating. But it is impossible to prepare pure hydrobromic acid by heating a mixture of potassium or sodium bromide with

concentrated sulphuric acid, because a portion of the hydrobromic acid which is set free reduces some of the sulphuric acid, forming bromine, water, and sulphurous anhydride, thus :—

$$\underset{\text{Hydrobromic acid}}{2HBr} + \underset{\text{Sulphuric acid}}{SO_2\begin{cases}OH\\OH\end{cases}} = Br_2 + 2H_2O + \underset{\text{Sulphurous anhydride}}{SO_2.}$$

The hydrobromic acid prepared in this way is, therefore, always coloured red with bromine gas, and is contaminated with sulphurous anhydride.

The pure, colourless gas may be easily prepared by decomposing phosphorous bromide with water, phosphorous acid being at the same time produced :—

$$\underset{\text{Phosphorous bromide}}{PBr_3} + 3H_2O = \underset{\text{Phosphorous acid}}{PHO\begin{cases}OH\\OH\end{cases}} + \underset{\text{Hydrobromic acid}}{3HBr.}$$

For this purpose, 1 part by weight of amorphous phosphorus is mixed with 2 parts of water, and then 10 parts of bromine gradu-

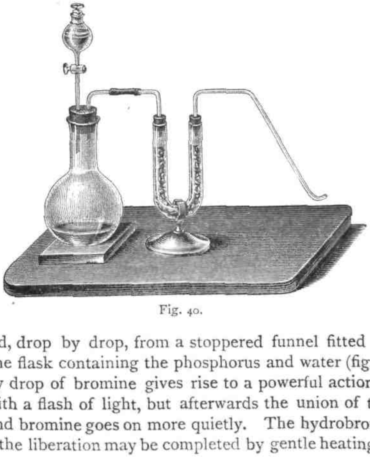


Fig. 40.

ally added, drop by drop, from a stoppered funnel fitted into the cork of the flask containing the phosphorus and water (fig. 40). At first every drop of bromine gives rise to a powerful action, accompanied with a flash of light, but afterwards the union of the phosphorus and bromine goes on more quietly. The hydrobromic acid, of which the liberation may be completed by gentle heating, is freed

from small quantities of bromine by passing it through a U-tube containing fragments of glass and ordinary phosphorus.

Hydrobromic acid is easily and completely decomposed by chlorine. If a cylinder of the dry gas is placed mouth to mouth with one containing dry chlorine, hydrochloric acid and bromine are produced, the latter being recognized by its brown colour. If the chlorine is in excess the brown colour disappears again, and bromine chloride is produced as a reddish-yellow mobile liquid.

In the same manner as hydrobromic acid, all bromides are also decomposed by chlorine. If chlorine water is added to a solution of a bromide, bromine will be set free, and may be easily recognized by its yellow or brown colour. If then a drop of carbon disulphide is added and the mixture shaken, this substance will dissolve the bromine and its colour will become more marked. Hydrobromic acid and all soluble bromides give a pale yellow precipitate of silver bromide when mixed with silver nitrate. The precipitate only dissolves in ammonia with difficulty.

OXY-ACIDS OF BROMINE.

In the same manner as chlorine, bromine cannot combine directly with oxygen. The combination may be brought about in an indirect manner, but no compounds of bromine and oxygen alone are known.

Bromic Acid: $BrO_2 \cdot OH$.—The potassium salt of this acid is produced, together with potassium bromide, when bromine is dissolved in concentrated caustic potash :—

$$\underset{\text{Caustic potash}}{6KOH} + 6Br = \underset{\text{Potassium bromate}}{BrO_2 \cdot OK} + \underset{\text{Potassium bromide}}{5KBr} + 3H_2O.$$

And as the potassium bromate, like potassium chlorate, is much less soluble in water than the bromide, it may be easily obtained pure by repeated crystallization. When heated, the salt breaks up into potassium bromide and oxygen.

Bromic acid—which may be separated from potassium bromate according to the method given on p. 110 for chloric acid—is a colourless, powerfully acid liquid, which first reddens and then

bleaches litmus paper. At 100° it decomposes into bromine and oxygen.

Hypobromous Acid: BrOH, may be obtained by shaking bromine water with precipitated mercuric oxide. The aqueous solution is a pale yellow liquid, which acts as a powerful oxidizer, and which bleaches like hypochlorous acid.

If bromine is allowed to evaporate at the ordinary temperature under a bell-jar with slaked lime, *bromide of lime* is obtained, a substance which resembles chloride of lime, and which also possesses bleaching properties.

IODINE.

Chemical Symbol: I.—*Atomic Weight*: 126·8.

Up to the commencement of the present century soda was exclusively prepared by burning sea-plants, extracting the burnt mass (called kelp, or varec) with water, and crystallizing the soda from the solution so obtained. The French chemist Courtois, when attempting to obtain chlorine from the residues of the above process by heating them with manganese peroxide and sulphuric acid, noticed a splendid violet vapour, the investigation of which led him to the discovery of iodine (1811).

The chemical nature of this element was, however, first made clear by the investigations of Gay-Lussac four years later. It owes its name to the colour of its gas (ἰώδης = violet-coloured).

Like chlorine and bromine, iodine does not occur free in nature, but always in combination with some of the metals. Sodium iodide is almost always present in common salt, although in extremely small quantities. Even those mineral springs which contain sodium chloride, and which are, comparatively speaking, rich in sodium iodide, contain such small quantities of iodine that its presence can scarcely be detected without concentration.

Sea-water contains even smaller quantities of sodium iodide, and yet this is the source from which by far the greatest proportion of the 100 tons of iodine which is consumed annually is obtained. But if we were obliged to procure iodine directly from sea-water,

the process would certainly be an unprofitable one ; we therefore extract it in an indirect manner with the aid of organic nature. Sea-plants, and particularly sea-weeds, extract the iodine from the sea-water and concentrate it in their structures, and it is from these plants alone that it is profitable to extract iodine by chemical processes. The manufacture is carried on principally on the west coasts of Britain (especially Scotland) and France. The sea-weeds are gathered during low water, dried and burnt, and the ashes thus obtained (called *kelp*) are rich in sodium iodide.

Not only the Algæ, but also other sea plants, take up iodine from the sea, and the same is true of many marine animals—the sponges, &c. In this way iodine is conveyed into the bodies, and especially into the fat, of many other marine animals, and occurs, for example, in ordinary cod-liver oil. In the mineral kingdom iodine is found as silver iodide in Peru, Mexico, &c., and as sodium iodide in those salt deposits which are due to the evaporation of sea-water. So, for example, in rock salt, and particularly in Chili saltpetre, or sodium nitrate occurring in Chili. From the mother-liquors of the crude sodium nitrate very considerable quantities of iodine are now manufactured.

Iodine is a solid crystalline substance, with a dark grey colour and metallic lustre. It neither conducts electricity nor heat ; it is brittle, and may be easily powdered, and possesses a peculiar, unpleasant odour, similar to that of chlorine and bromine, but less intense. It melts at 113°, forming a dark brown liquid, boils at about 200°, and gives off a dark violet-coloured vapour. On cooling, the walls of the vessel become covered with innumerable small, lustrous crystals of the solid. Its specific gravity is 4·95, and that of its vapour 8·7 compared with air as unity. Its molecular weight is thus $8{\cdot}7 \times 28{\cdot}88 = 251$; whence it follows that its molecule, like that of hydrogen, consists of two atoms. (See Appendix.)

Although iodine only boils at about 200°, it is so volatile at the ordinary temperature that when left exposed to the air it soon loses considerably in weight ; and when kept in closed vessels it sublimes, like camphor, on to the cooler portions of the bottle. It is slightly soluble in water, much less than chlorine and bromine, and forms a yellow-brown solution. It possesses a strong unpleasant taste, colours the skin yellow, and is poisonous.

Water containing salts dissolved in it, particularly potassium iodide, dissolves larger quantities of iodine than pure water ; it is

also dissolved in considerable quantities by aqueous hydriodic acid. Alcohol and ether, as well as chloroform and carbon disulphide, are good solvents of iodine. Its alcoholic solution possesses a dark brown colour and is called *tincture of iodine*. The solution in ether is also of a brown colour, while that in chloroform or carbon disulphide is dark violet, or when largely diluted a bright pink.

Many applications are made of iodine in medicine and in the arts—for example, in photography. Tincture of iodine is applied externally to reduce goitre, enlarged joints, and other similar swellings, and potassium iodide is taken internally to produce the same effect. Long before this action of the salt was known, even before iodine itself was discovered, the ashes obtained by burning sponges were used as a medicine for these diseases. It was later found that these ashes contain sodium iodide, and since then potassium iodide or sodium iodide has always been used in these cases.

The preparation of iodine from the aqueous extraction of the ashes of sea-plants after most of the soda and common salt have crystallized out, or from the mother-liquors of Chili saltpetre, may be carried out by passing chlorine through the liquid, which separates the iodine. Care must be taken that too much of the gas is not passed, otherwise iodine chloride will be produced, which diminishes the yield. Another method is to heat the crude substances in iron or earthenware vessels with only just enough sulphuric acid and manganese peroxide to decompose the sodium iodide present. This salt is more easily decomposed than the chloride, and consequently the iodine separates first before the chlorine. The process is similar to that used for the preparation of chlorine (p. 100), substituting iodine for chlorine :—

$$2NaI + MnO_2 + 3SO_2\begin{cases}OH\\OH\end{cases} =$$

$$2SO_2\begin{cases}OH\\ONa\end{cases} + SO_2{\cdot}O_2Mn + 2H_2O + I_2.$$

The iodine vapour is received in a number of communicating vessels to condense it, then freed from water and purified by resublimation. Usually the two methods are employed together. The iodine is first separated by chlorine, excess being avoided, again converted into sodium iodide by caustic soda and then distilled with manganese peroxide and sulphuric acid. Commercial iodine not unfrequently contains iodine chloride and cyanide ; it

may be purified, in the same manner as bromine (p. 120), by distilling with potassium iodide :—

$$\underset{\text{Iodine chloride}}{ICl_3} + \underset{\text{Potassium iodide}}{3KI} = \underset{\text{Potassium chloride}}{3KCl} + 2I_2.$$

In its chemical properties iodine exhibits close analogy with chlorine and bromine. It has, however, less affinity for the metals and for hydrogen than these two elements, which therefore expel iodine from its soluble salts and from its compound with hydrogen—hydriodic acid. On the other hand, iodine has a stronger affinity for oxygen than the other two halogens ; iodic acid, for example, is a solid substance easily crystallized and much more stable than the corresponding chloric and bromic acids.

The behaviour of iodine to starch is very remarkable. Thin starch paste mixed with an aqueous solution of iodine becomes of a dark blue colour, which, however, vanishes on warming. It appears as if a real chemical compound were produced by this reaction, but no attempt to determine its composition has been yet successful. The colour is only produced by free iodine, and not by solutions of its salts, and starch paste can therefore be mixed with potassium iodide in any proportion without producing any change in colour. But if to the mixture a drop of chlorine water is added, which sets iodine free, a dark blue coloration is at once noticed.

This property is employed both to detect traces of starch and of free iodine. If a piece of paper moistened with starch is hung up in a closed cylinder containing a few drops of a liquid with free iodine at the bottom, the paper soon becomes blue owing to the vapours of iodine rising from the liquid.

More delicate even than this reaction, and therefore applicable to the detection of infinitesimal quantities of iodine, is the pink or purple colour which traces of iodine impart to chloroform or to carbon disulphide. Chlorine water is not well adapted for the separation of minute quantities of iodine from a liquid, as the slightest excess unites at once with the separated iodine to form iodine chloride. It is better in such a case to employ fuming nitric acid. A few drops of this acid added to the liquid to be tested and well shaken up with it in a glass cylinder suffice to convert the iodide into a nitrate and set hydriodic acid free ; this at once gives up its hydrogen to the loosely combined oxygen of the nitric peroxide contained in the fuming nitric acid and sets iodine free :—

$$\underset{\text{Hydriodic acid}}{4HI} + \underset{\text{Nitric peroxide}}{N_2O_4} = 2I_2 + 2H_2O + \underset{\text{Nitric oxide}}{2NO.}$$

If a little chloroform or carbon disulphide is then added and the liquid well shaken, the former after settling to the bottom of the cylinder becomes pink coloured, even if only traces of iodine are present. When, on the other hand, iodine is completely absent, the chloroform or carbon disulphide remains colourless.

HYDRIODIC ACID.

Composition: HI.

Like hydrochloric and hydrobromic acids, this compound is a colourless gas, fuming in the air, with an acid taste and piercing odour, and is very easily absorbed by water. In the same manner as hydrochloric acid, it consists of one volume hydrogen united with one volume iodine vapour to form two volumes of the compound without condensation. Its vapour density ($H = 1$) is, therefore, $\frac{127 + 1}{2} = 64$, or compared with air as unity 4·4.

In consequence of the high specific gravity of iodine gas and the low specific gravity of hydrogen, the weight of the hydrogen contained in hydriodic acid is so small, that it was for some time overlooked. From the formulæ we see that $127 + 1 = 128$ parts by weight of hydriodic acid only contain one part by weight of hydrogen, or less than one per cent.; the exact percentage being $\frac{1 \times 100}{128} = 0{\cdot}78$.

The affinity of iodine for hydrogen is even less than that of bromine for the same substance. Hence hydriodic acid cannot be prepared by the direct union of its elements. (See App.) Neither can it be prepared pure by decomposing potassium iodide with concentrated sulphuric acid. Large quantities of hydriodic acid are, it is true, set free by this reaction, but the gas is largely contaminated with iodine, because the hydriodic acid is decomposed at the moment of its production by the excess of sulphuric acid into iodine, water, and sulphurous acid.

In order to prepare pure hydriodic acid we can only use one

method—viz. the decomposition of phosphorous iodide by water. In order to form this compound ordinary (yellow) phosphorus and iodine are made to combine in the proportion of one equivalent of the former to three equivalents of the latter—*i.e.* in the proportion of 31 parts of phosphorus to $3 \times 127 = 381$ parts of iodine, or 1 part to 12·3 parts. But as it is better to have the phosphorus in slight excess, 1 part of phosphorus is mixed with 10 parts of iodine. The proper quantity of iodine is weighed off into a dry flask, the flask filled with carbonic acid, and then the requisite quantity of phosphorus, cut into small pieces and dried, is gradually added. The two bodies unite immediately with one another, producing flashes of light, to form liquid phosphorous iodide. In order to distribute the excess of phosphorus uniformly through the mass, the compound is gently heated and kept in a molten state for a short time.

After the compound has cooled and solidified to a crystalline mass, it is moistened with a little water and gently warmed. Phosphorous acid and hydriodic acid are produced, and the latter passes away through a tube fitting in an india-rubber stopper in the neck of the flask. It may be led into water if an aqueous solution of the gas is to be prepared. The delivery tube must be wide, otherwise it is apt to become plugged up for the following reason. Phosphorous acid is decomposed on heating into phosphoric acid and phosphoretted hydrogen, and this decomposition is greatest, the smaller the quantity of water present. But phosphoretted hydrogen and hydriodic acid, when in contact with one another, unite to form a solid crystalline substance of the composition: $PH_3 \cdot HI = PH_4I$ (phosphonium iodide). In the preparation of hydriodic acid this compound may be easily formed, and the delivery tube may become plugged with crystals of it.

Aqueous hydriodic acid is a colourless liquid with a strong acid reaction and odour. If completely saturated with the gas in the cold, it fumes when exposed to the air. When kept in vessels containing air, especially when exposed to the light, the solution soon becomes of a yellow or brown colour, from the iodine liberated by the oxidation of the hydrogen. The weak affinity with which the hydrogen and iodine are combined together is apparent from the fact that when a glass rod is heated in the flame, and plunged into a jar of the gas, violet vapours of iodine are at once produced. If the rod was red-hot, the liberated hydrogen often catches fire.

Chlorine and bromine decompose hydriodic acid and all the

iodides (except silver iodide) very easily. If a jar of chlorine is inverted over one of hydriodic acid gas, and then the position of the jars reversed, so that the heavier hydriodic acid comes uppermost, a considerable quantity of heat is produced, and iodine is set free, with the production of hydrochloric acid. If the chlorine is in excess, the iodine soon disappears, uniting with the chlorine to form iodine chloride.

Hydriodic acid and the soluble iodides produce with silver nitrate a yellow precipitate of silver iodide, which is almost insoluble in ammonia.

OXY-ACIDS OF IODINE.

Of the oxygen compounds of iodine only two are well known—iodic acid and periodic acid—which correspond in their composition to chloric acid and perchloric acid.

Iodic Acid : $IO_2 \cdot OH$.

This compound is distinguished from the unstable chloric acid by its comparative stability. It is a solid, and crystallizes in hexagonal plates ; is soluble in water and in alcohol, and possesses a bitter acid taste. It may be heated to above 100° without being essentially changed ; at a higher temperature it is decomposed into water and iodic anhydride—I_2O_5.

Iodic acid may be prepared by the direct oxidation of iodine by nitric acid, if too large quantities are not employed at one time. About 10 grammes of iodine are finely powdered and gently heated in a capacious flask with twice as much *concentrated* nitric acid. As soon as no further action takes place the acid liquid is poured off, and the residue digested with a fresh quantity of nitric acid until all iodine has disappeared. As iodic acid is only slightly soluble in nitric acid, the greater portion remains behind in the flask as a crystalline powder ; the acid liquid is poured off and evaporated to dryness, when a further quantity of iodic acid is obtained. Both portions are then dissolved in water, evaporated to dryness, to expel the last traces of nitric acid, and, finally, heated to 100°—130° in a stream of dry air.

An aqueous solution of iodic acid does not yield large crystals of the acid when evaporated down, but such crystals may be

easily obtained by adding a little nitric or sulphuric acid, and then evaporating.

Barium iodate is decomposed when boiled with dilute sulphuric acid into insoluble barium sulphate and iodic acid. If the clear liquid is filtered off, crystals of iodic acid separate on evaporation. At the ordinary temperature sulphuric acid has but little action on the barium salt. To prepare iodic acid by this process, two parts of concentrated sulphuric acid diluted with eight parts of water are allowed to act upon nine parts of the finely-powdered barium salt.

If iodine is boiled with caustic potash, the solution contains potassium iodide and potassium iodate—just as when chlorine acts upon a hot concentrated solution of caustic potash—and the iodate, being less soluble than the iodide, crystallizes out first on evaporation. In a solution of potassium iodate, barium chloride produces a white precipitate of the difficultly soluble barium iodate. This salt may also be directly prepared by boiling iodine with concentrated baryta water.

Iodic acid when heated up to 130°, or slightly higher, loses water and becomes converted into a compound having the composition $I_3O_7 \cdot OH$, which may be considered as one molecule of iodic acid united with one molecule of iodic anhydride—*i.e.* $IO_2OH + I_2O_5$. It is distinguished from iodic acid by its insolubility in ordinary alcohol. If iodic acid is heated still higher, up to 170°, it loses a further quantity of water, and is completely converted into the anhydride, I_2O_5. The decomposition is also produced by absolute alcohol, or by a mixture of this substance with sulphuric acid.

Iodic Anhydride: I_2O_5 or $\left.\begin{matrix} IO_2 \\ IO_2 \end{matrix}\right\} O$.

This compound is easily soluble in water, and then reproduces iodic acid. When strongly heated—up to about 300°—it is decomposed into iodine and oxygen.

Although the oxygen in iodic acid is much more firmly combined than in chloric or bromic acid, the acid still easily gives up its oxygen to those substances which exercise a reducing action, and is therefore a powerful oxidizing agent. Sulphurous acid and sulphuretted hydrogen, when added to a dilute aqueous solution of iodic acid, cause an immediate separation of iodine; nitrous acid, phosphorous acid, and other substances produce the same result.

With dry hydrochloric acid gas, dry iodic anhydride yields iodine chloride, chlorine, and water :—

$$I_2O_5 + 10HCl = 2ICl_3 + 2Cl_2 + 5H_2O.$$

Iodic acid is a monobasic acid, and produces salts which are mostly insoluble in water. It shows a strong tendency to form so-called acid salts besides the neutral compounds. The acid salts may be considered as neutral salts united with one or two molecules of the acid. We know, for example, the following three potassium compounds :—

Normal potassium iodate .	. IO_2OK.
Monacid potassium iodate .	. $IO_2OK + IO_2OH$.
Diacid potassium iodate .	. $IO_2OK + 2IO_2OH$.

Like the chlorates, the iodates of the metals are decomposed on heating into iodides and oxygen—the iodates of the heavy metals usually giving up iodine as well, and becoming converted into oxides. It is not, however, possible to expel all the oxygen from potassium iodate by heating it even to redness.

Iodic acid possesses the remarkable property of uniting chemically with strong acids. If dry and powdered iodic acid is gradually added to about five times its weight of hot concentrated sulphuric acid, a substance separates out on cooling which contains both acids chemically united.

Periodic Acid : $IO_3 \cdot OH + 2H_2O$, or $IO(OH)_5$.

The monobasic acid is unknown in the free state ; we are only acquainted with its compound, with two molecules of water, which may be considered as a pentabasic acid. This substance crystallizes in colourless rhombic prisms, which are soluble in water, alcohol, and ether, and deliquesce when exposed to the air. The aqueous solution may be boiled without causing decomposition, and the crystals are not altered by standing in a desiccator over sulphuric acid. At a temperature of 133° the acid melts, and begins to be decomposed into water, oxygen, and iodic anhydride at 140°.

Four kinds of periodic acid are known in its salts, which are mono-, tri-, tetra-, and pentabasic respectively. These acids may be represented as compounds of the unknown periodic anhydride :

I_2O_7, containing heptad iodine, with varying proportions of water thus :—

$$I_2O_7 + H_2O \ldots\ldots = 2IO_3 \cdot OH.$$
$$I_2O_7 + 2H_2O \ldots\ldots = O\begin{cases} IO_2(OH)_2. \\ IO_2(OH)_2. \end{cases}$$
$$I_2O_7 + 3H_2O \ldots\ldots = 2IO_2(OH)_3.$$
$$I_2O_7 + 5H_2O \ldots\ldots = 2IO(OH)_5.$$

Of these acids the last-named is known in the free state, but the others only in their salts.

Pentabasic periodic acid may be obtained in the following way. When chlorine is led into a hot solution of sodium iodate, containing free caustic soda, an acid sodium salt of the pentabasic periodic acid is produced according to the equation :—

$$IO_2 \cdot ONa + 3NaOH + Cl_2 = IO\begin{cases} (ONa)_2 \\ (OH)_3 \end{cases} + 2NaCl.$$

This sodium salt, which is nearly insoluble in water dissolves in nitric acid, and gives with silver nitrate a precipitate of the corresponding silver salt, which when evaporated down with nitric acid, is converted into yellow crystals of the silver compound of the monobasic acid : $IO_3 \cdot OAg$. Finally, if this salt is boiled with water, the former silver compound is again produced, and the pentabasic acid set free :—

$$2IO_3 \cdot OAg + 4H_2O = IO\begin{cases} (OAg)_2 \\ (OH)_3 \end{cases} + IO(OH)_5.$$

The solution is then filtered and evaporated down to crystallize.

The normal silver salt of the pentabasic acid, $IO(OAg)_5$, has also been prepared, as well as the sodium salt of the tetrabasic acid : $O\begin{cases} IO_2(ONa)_2 \\ IO_2(ONa)_2 \end{cases}$, by heating the above acid salt to 220°—

$$2IO\begin{cases} (ONa)_2 \\ (OH)_3 \end{cases} = O\begin{cases} IO_2(ONa)_2 \\ IO_2(ONa)_2 \end{cases} + 3H_2O.$$

As will be seen from the above formulæ, the composition of the periodates is very various and somewhat complex. Similar compounds are known of the oxy-acids of sulphur and phosphorus, which have been subjected to more exact investigation than the periodates.

Chlorides of Iodine.

Chlorine and iodine unite together to form two compounds—iodine monochloride, and iodine trichloride.

Iodine monochloride: ICl, is a red-brown liquid, which crystallizes on standing, and which possesses the odour of both iodine and chlorine. The crystals melt at 25°; they are soluble in water, whence they may be again extracted by shaking with ether.

Iodine monochloride is prepared by heating together one part of iodine with four parts of potassium chlorate, or by dissolving iodine in aqua regia, diluting with water and extracting with ether. It then remains behind on allowing the ethereal solution to evaporate. It may also be prepared by acting upon one molecule of iodine trichloride with one molecule of iodine :—

$$ICl_3 + I_2 = 3ICl.$$

Iodine trichloride: ICl_3, crystallizes as yellow needles when chlorine is led over gently heated iodine; if it contains iodine monochloride its colour is more or less of a brownish tint. On heating, it melts and becomes brown, being decomposed into chlorine and iodine monochloride.

FLUORINE.

Chemical Symbol: F.—*Atomic Weight*: 19.

Fluorine occurs in nature mainly as fluor-spar: CaF_2, and cryolite: Na_3AlF_3 or $6NaF.Al_2F_6$, and to a less extent in certain other minerals.

Owing to its powerful chemical affinities for other elements, and the fact that it attacks all the materials of which chemical vessels are composed, most of the attempts that have been made to prepare this element in the free state have failed. In 1886, however, Moissan succeeded in isolating it, by passing an electric current through a solution of hydrogen potassium fluoride in anhydrous hydrofluoric acid. This solution, which must be absolutely free from water, which is at once decomposed by fluorine, is prepared by distilling hydrogen potassium fluoride, which has been previously dried as far as possible. The first portion of the distillate, which contains any residual water, is neglected. The small quantity of alkaline fluoride which is mechanically carried over with the hydrofluoric acid is of advantage, in that it renders the latter a better conductor of electricity. The electrolytic decomposition is carried out in a **U** tube, made of an alloy of platinum and iridium.

The fluorine separates at the positive pole as a colourless gas possessing a disagreeable odour, and which readily enters into combination with most other elements. Of the halogens, fluorine has the greatest affinity for hydrogen, combining with it even in the dark (chlorine only in direct sunlight). Sulphur, selenium, phosphorus, iodine, crystalline silicon, and boron, each burn when placed in this gas, and potassium, sodium, calcium, &c., severally become incandescent under similar treatment. Fluorine does not appear, however, to have any action upon the comparatively inert element carbon, and it is noteworthy that it has been found impossible to prepare an oxide of fluorine. It differs in this respect from all other elements, this peculiarity being in accordance with the fact that fluorine is, like oxygen, a strongly electro-negative element, and immediately follows oxygen in the electro-chemical series of the elements.

HYDROFLUORIC ACID (*Fluoric Acid*).

Composition: HF.

This compound is a colourless gas with a piercing acid odour, and may be condensed by cold to a colourless liquid boiling at 19° and not solidifying at $-34°$. The gas acts very injuriously upon the lungs and air passages when breathed in small quantities, and in larger quantities may produce death. Like hydrochloric acid, the gas fumes powerfully in the air, and is also energetically absorbed by water with considerable evolution of heat. If led into a vessel of water which is kept cool, as long as absorption takes place a fuming aqueous solution is produced, which gives off hydrofluoric acid when heated. At the same time the boiling-point gradually rises and at last remains constant (under the normal atmospheric pressure) at 120°. The aqueous hydrofluoric acid, which distils over at this temperature, contains about 36 per cent. of the gas by weight.

As all siliceous substances are decomposed by hydrofluoric acid, with the production of silicon fluoride, the acid cannot be prepared in glass or porcelain vessels. It is best to employ vessels of platinum, which is not in the least attacked by the acid, or of lead, upon which it only slightly acts. A very convenient apparatus is made of lead, and has a platinum tube fastened airtight into it to conduct the gas into water contained in a platinum vessel (fig. 41).

The vessel which serves as the retort is a cylinder of lead, on

which fits a cap of the same metal, and which is pierced by a hole at the side to receive the platinum tube. Finely powdered fluorspar is mixed with concentrated sulphuric acid in the vessel to about the consistency of cream, the cap is placed on and made tight with plaster of Paris, and, finally, the platinum tube is fixed in position and also cemented with plaster. As soon as the plaster has set the cylinder is placed on an iron plate and gently warmed. The tube is so arranged that it just touches the surface of the water which is to absorb the gas, and which is contained in a platinum crucible. The crucible must be surrounded with ice or

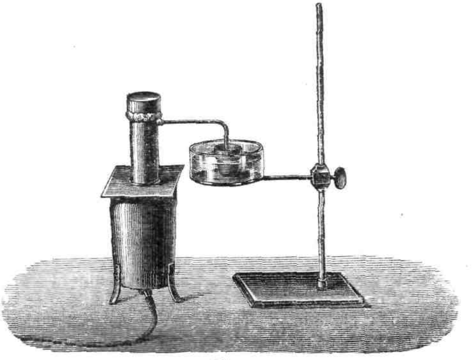


Fig. 41.

cold water in order to keep it cool. By means of this simple apparatus, concentrated aqueous hydrofluoric acid may be quickly obtained at any time.

To prepare the gas perfectly pure and absolutely dry it is best to employ the compound which is produced by acting on potassium fluoride with hydrofluoric acid. This substance, which has the composition KHF_2, decomposes again when heated in a platinum vessel into potassium fluoride and hydrofluoric acid.

Fluorine in combination with hydrogen and with most of the metals plays the part of a monad element. But in certain double fluorides (*e.g.* the potassium compound just referred to) it appears

as if two atoms of fluorine coalesced to form a diad, and this compound would have a composition analogous to that of potassium hydrate, thus :-

Potassium hydrate	$KO''H$.
Hydric potassium fluoride . . .	$KF_2''H$.

By the union of hydrofluoric acid with bases the fluorides are produced. Many of the fluorides are soluble in water, and to these belongs the silver salt. In this respect hydrofluoric acid differs from the otherwise similar acids, hydrochloric, hydrobromic, and hydriodic acids, which form insoluble silver salts. On the other hand, the fluorides of some metals (*e.g.* calcium), which form very soluble chlorides, bromides, and iodides, are quite insoluble in water.

One of the most important properties of hydrofluoric acid, in which it is again distinguished from the other halogen acids, is its decomposing action on silica and the silicates. No other acid, not even sulphuric acid or phosphoric acid, attacks silica, while hydrofluoric acid dissolves it, forming gaseous silicon fluoride and water :—

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

If the silica is united with bases, as, for example, in common glass with lime and soda, the corresponding fluorides are produced by the action of the acid.

We make use of this property not only to test for hydrofluoric acid, but also to etch glass—for example, to mark a series of divisions on a glass tube. The operation for either of these purposes is as follows : Fluor-spar, or the substance to be examined for fluorine, is finely powdered, placed in an open platinum crucible, mixed with concentrated sulphuric acid, and, if necessary, very gently warmed. A watch-glass is then taken and its convex side covered with a thin layer of wax, by warming it gently and rubbing it over with a piece of wax. As soon as the glass is cold the characters which are to be etched are written on the waxed surface with a sharply-pointed piece of slate-pencil, which removes the wax at those points where it touches the glass. If the watch-glass so prepared is now placed over the crucible with its convex side downwards, the glass becomes corroded at those points which are not protected by the layer of wax, and only at those points. By the action of the hydrofluoric acid on the glass, silicon fluoride, sodium fluoride, and calcium fluoride are produced. The first-

named substance passes away as a gas, the second is removed by subsequent washing with water carrying the third mechanically with it.

If the glass is removed after remaining for a short time over the crucible, washed with water and the wax removed by warming, the characters traced on the glass become distinctly visible, in consequence of the contrast between those parts of the glass which have been etched and those which were unacted upon by the acid.

For the production of delicate and exactly equal divisions on glass tubes and other similar etchings, it is best to employ the commercial aqueous acid, which only fumes slightly in the air. The divisions having been marked on the waxed tube, this aqueous acid is painted on the parts to be etched with a camel's hair brush.

The fact that hydrofluoric acid etches glass was observed two hundred years ago by Schwankhard of Nuremberg—*i.e.* he found that a mixture of fluor-spar and sulphuric acid corroded glass. But it was only a hundred years later that Scheele, the discoverer of chlorine, showed that this action is due to a gas given off by this mixture, and the composition of this gas was first discovered by Ampère at the commencement of the present century.

Gutta-percha, like wax, is neither attacked nor dissolved by hydrofluoric acid, and the aqueous acid can therefore be preserved and transmitted from one place to another in bottles of gutta-percha provided with stoppers of the same substance.

ELEMENTS OF THE SULPHUR GROUP.

To this group belong the three elements, sulphur, selenium, and tellurium. They form a natural group similar to those referred to on p. 65. All three are solid and crystalline; they can be easily melted and sublimed, and are combustible. Selenium and tellurium are distinguished from sulphur by their metallic lustre. Their chemical nature is interesting from the fact that they can form two distinct classes of compounds in which they play different parts. On the one hand, they so closely resemble oxygen that they can partially or entirely displace this element from its compounds; on the other hand, they combine with oxygen itself to

form compounds usually possessing acid properties, and in which they have the same relation to oxygen as phosphorus has in its acids and arsenic in its acids.

In all cases where they take the place of oxygen, their atomicity, like that of this element, is always two, while in their compounds with oxygen they offer four or six points of attraction to this element.

When sulphur, which may be here considered as a representative of the entire group, enters into chemical combination as a diad, the compounds produced—sulphides—exhibit a close chemical relationship to the corresponding oxides. Thus :—

Water	H_2O
corresponds to	
Sulphuretted hydrogen	H_2S.
Arsenious oxide	As_2O_3
corresponds to	
Arsenious sulphide	As_2S_3.
Potassium hydrate	KOH
corresponds to	
Potassium sulphydrate	KSH.
Cupric oxide	CuO
corresponds to	
Cupric sulphide.	CuS.

Arsenious oxide and arsenious sulpide possess acid properties while potassium hydrate and sulphydrate, cupric oxide, and sulphide, are bases.

Potassium arsenite is produced by the union of arsenious oxide and caustic potash, and, in the same manner, from arsenious sulphide and potassium sulphydrate potassium sulpharsenite is formed :—

$$As_2O_3 + 2KOH = 2AsO \cdot OK + H_2O,$$
$$As_2S_3 + 2KSH = 2AsS \cdot SK + H_2S.$$

So, too, arsenious oxide and cupric oxide unite to form cupric arsenite, while the union of arsenious sulphide and cupric sulphide produces cupric sulpharsenite; the sulphur compounds containing in every case sulphur instead of oxygen.

But when the elements of the sulphur group are united with oxygen to form the radicals of the oxy-acids, their chemical character is entirely different. In the compounds of diad sulphur

this element can always be displaced by oxygen; but this is not possible in the second class of compounds, in which the sulphur exists as a tetrad or hexad element combined with oxygen, because, as far as we know, oxygen only exists as a diad element, and never possesses any higher atomicity. We might imagine the existence of a compound corresponding to sulphurous anhydride—$S^{iv}O_2$—in which the two atoms of diad oxygen might be displaced by two atoms of diad sulphur—$S^{iv}S^{ii}_2$, and the sulphur which is set free by the action of sulphuretted hydrogen on sulphurous anhydride is perhaps this sulphur:—

$$S^{iv}O_2 + 2H_2S^{ii} = S^{iv}S^{ii}_2 + 2H_2O.$$

But we cannot imagine the existence of a similar compound in which the tetrad sulphur of sulphurous anhydride is displaced by tetrad oxygen, $O^{iv}O^{ii}$, because, as far as we know, oxygen never plays the part of a tetrad.

The composition of thiosulphuric acid proves that the displacement of oxygen in the oxy-acids, by diad sulphur, is not only possible, but actually takes place. This acid is sulphuric acid, $S^{vi}O_2\begin{cases}OH\\OH\end{cases}$, in which one of the atoms of oxygen united with the hydrogen is displaced by an atom of diad sulphur, thus: $S^{vi}O_2\begin{cases}S^{ii}H\\OH\end{cases}$.

These facts are not only true for sulphur compounds, but may be generally extended to those of selenium and tellurium.

Selenium and tellurium may be said to occur as rarely in nature as sulphur does abundantly. These two elements (particularly selenium) very often occur associated with sulphur. And their scarcity is probably the reason why their compounds have not been so thoroughly investigated as those of sulphur.

SULPHUR.

Chemical Symbol: S.—*Atomic Weight*: 32·1.

Sulphur occurs free in nature in considerable quantities; Sicily and other parts of Italy as well as Iceland are particularly rich in native sulphur. It is still more widely distributed in chemical combination with other bodies. Of the sulphides, the commonest

are *iron pyrites* (ferric disulphide, FeS_2), *copper pyrites* (copper-iron sulphide, $CuFeS_2$), *galena* (lead sulphide, PbS), *blende* (zinc sulphide, ZnS), &c. Sulphur is not less common in combination with calcium and oxygen, as calcium sulphate, in the mineral *gypsum* ($SO_2 \cdot O_2Ca + 2H_2O$), which often occurs in layers of considerable thickness. Other sulphates are also found in nature, among which may be mentioned *Glauber's salt* (sodium sulphate, $SO_2(ONa)_2$, *Epsom salt* (magnesium sulphate, $SO_2 \cdot O_2Mg$)—two compounds which are contained in mineral waters and in sea water. Other naturally occurring sulphates are, *heavy-spar* (barium sulphate, $SO_2 \cdot O_2Ba$), *alunite* (basic aluminium-potassium sulphate), &c. Besides all these forms in which sulphur is found in nature, it also forms a constituent of many important organic substances, such as albumen.

Few substances are so generally known as sulphur, and yet the outside world is but little acquainted with its remarkable physical and chemical properties.

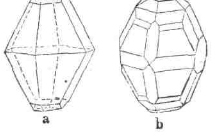
Sulphur is a brittle, crystalline solid, with a pale yellow colour, without taste or odour, quite insoluble in water, and only slightly soluble in alcohol and ether. It is, however, dissolved by carbon disulphide in large quantities, especially when the liquid is heated to its boiling point.

At 115° it melts to a clear mobile liquid of a pale yellow colour, which easily resolidifies to ordinary yellow sulphur, but which if more strongly heated (up to 200°) undergoes a remarkable change. It does not become more mobile, as might be expected, but more and more viscid, and at the same time darker and darker in colour. At 200° it is a dark-brown liquid so viscid that the vessel containing it may be inverted without any of it running out. When heated above 200°, up to 400°, the liquid gradually becomes mobile again, without appreciably changing its colour, and boils at 448°. The sulphur gas which is so produced and fills the vessel has a dark red-brown colour, somewhat resembling gaseous bromine.

Sulphur which has been heated up to 200° possesses altogether other properties than the normal liquid sulphur at 115°. If the latter be cooled, for example, by pouring it into cold water, the original brittle yellow sulphur, soluble in carbon disulphide, is obtained. But if the sulphur at a temperature of 200°, or slightly higher, is poured into cold water, a tough, brown, elastic mass is produced, which may be drawn out into long threads and which only changes into ordinary yellow, brittle sulphur after some time.

This tough elastic modification of sulphur, unlike ordinary sulphur, is insoluble in carbon disulphide. Only after some time, or after it has been heated to 111° and allowed to cool again, does it regain its solubility in this liquid.

Sulphur is dimorphous—*i.e.* it crystallizes in two distinct forms. The transparent yellow crystals, as they occur in nature, belong to the rhombic system. The two accompanying figures (fig. 42) represent two common forms of native sulphur: the one (*a*) is simple, the other (*b*) has numerous secondary faces. Sulphur crystallized in the wet way—*e.g.* from its solution in carbon disulphide—shows exactly the same forms. Large regular crystals of rhombic sulphur may be obtained by heating a piece of sulphur with carbon disulphide in a sealed glass tube up to 120° or 130° and allowing it to cool slowly.[1] The crystals are afterwards freed from the carbon



a b

Fig. 42.

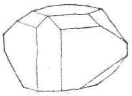


Fig. 43.

disulphide and dried, when they preserve their transparency and crystalline form unchanged.

On the other hand, when sulphur is melted and quickly cooled, it crystallizes in the monoclinic system (fig. 43). These crystals are best obtained by melting sulphur in a crucible at the lowest possible temperature, so that it remains mobile and does not pass into the viscid condition, allowing it to cool until a thin solid crust forms on the surface of the sulphur, then breaking a hole in this crust and pouring out the still liquid sulphur inside. If the crucible is broken up when cold the interior will be found filled with pale yellow needle-like prisms, often as much as an inch long. These crystals soon lose their transparency and become opaque and brittle; they then consist of a number of minute rhombic crystals similar in form to those in which sulphur occurs in nature, and in which it crystallizes from its solution in carbon disulphide. These

[1] The glass tube must be thick and well sealed up in the blowpipe, otherwise a very dangerous explosion may be produced.—ED.

two modifications of sulphur are also distinguished from one another by their different specific gravity. The specific gravity of natural or rhombic sulphur is 2·07, while that of the monoclinic modification is 1·96.

The vapour density of sulphur at different temperatures is remarkable. If the molecule of gaseous sulphur consisted, according to the general rule, of two atoms, its molecular weight would be $2 \times 32 = 64$, and its density $\frac{64}{28 \cdot 88} = 2 \cdot 216$ (p. 51). But the direct determination of the density of sulphur vapour at about 500°—a temperature considerably above its boiling point—gives quite a different number—viz. 6·654, or about three times 2·216. Further experiments undertaken to explain this anomaly showed that between the temperatures 440° and 850° sulphur vapour did not expand regularly with the increase of temperature, and that at 900° to 1,000° its density was only one-third of that at 500°, or about 2·216.

Sulphur, therefore, exists in two polymeric modifications in the gaseous state, which have different densities, and therefore different molecular weights. The vapour density of sulphur at 500° being 6·654, gives, when multiplied by 28·88, a molecular weight of 192, or 6×32 (S_6). These hexatomic molecules break up at a higher temperature, and at 900° the density becomes 2·216, which corresponds to a molecular weight of 64, or 2×32 (S_2). Each hexatomic molecule has thus been dissociated into three diatomic molecules by the rise in temperature.

Most of the sulphur which comes into trade is brought from Italy, and especially from Sicily, where the crude sulphur is partly melted out, and partly distilled in cast-iron vessels, from the earthy impurities. This sulphur is, however, still impure, and must be purified by distillation. For this purpose the arrangement shown in fig. 44 is employed. The sulphur is heated to boiling in the cast-iron retort G, which is built into the masonry, and of which the neck D opens into a large empty bricked chamber A. In the same manner as water vapour when cooled at once below its freezing-point condenses in the form of snow, so the sulphur vapour when issuing into the cold chamber at a temperature below its melting point condenses to sulphur snow, which collects on the walls and floor of the chamber. This light pale yellow sulphur-snow is the *flowers of sulphur* of commerce. But when the hot sulphur vapour has raised the temperature of the chamber to the melting-point of sulphur (115°) the sulphur melts and

collects on the floor as a thin liquid. It may then be allowed to flow out by an opening which can be regulated from the outside. This sulphur is nearly pure. Stick sulphur is easily obtained from it by running the liquid sulphur into wooden moulds (fig. 45). The sulphur gas which streams into the chamber is at a higher temperature than that necessary for the combustion of sulphur; it therefore unites with the oxygen contained in the air of the chamber and burns to form sulphurous anhydride, evolving at the same time a considerable quantity of heat. In consequence

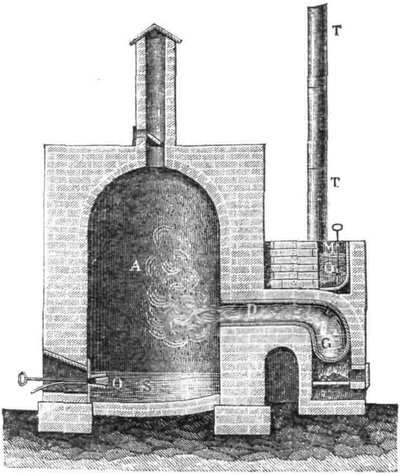


Fig. 44.

Fig. 45.

of this increase in temperature the whole of the air of the chamber suddenly expands, and the walls would not be able to withstand the increased pressure if the chamber were not furnished with a valve. This valve opens during the combustion of the sulphur and closes afterwards by its own weight.

The sulphurous anhydride which is now contained in the chamber is absorbed by the flowers of sulphur, and if this sulphur is afterwards brought into contact with moist air the sulphurous

anhydride is gradually oxidized to sulphuric acid. The sulphuric acid adheres so persistently to the flowers of sulphur that, even after repeatedly washing with water, sulphuric acid may be always recognized in the wash-water. For this reason flowers of sulphur moistened with water always redden blue litmus paper, which is not the case with stick sulphur.

Sulphur is also prepared by heating iron pyrites in a small supply of air, and remelting the sulphur, but the product so obtained is nearly always contaminated with arsenic.

All elements which unite with oxygen, either more or less energetically, also combine with sulphur and in nearly the same degree. And sulphur can also unite with oxygen itself. At the ordinary temperature the two elements do not unite with one another; but if sulphur is heated in the air, or in oxygen, it catches fire and burns with a pale blue flame, to form sulphurous anhydride. Besides this body there are several other compounds of sulphur and oxygen, of which sulphuric acid is the best known.

Sulphur unites directly with hydrogen, only with difficulty, and the compound of the two elements—sulphuretted hydrogen—is easily decomposed again. Chlorine and sulphur combine with one another when gently heated. Phosphorus unites with sulphur as readily as it does with oxygen, and two of the compounds produced correspond in composition to phosphorous and phosphoric anhydrides. Nitrogen and sulphur have only a weak affinity for one another, and only combine under peculiar circumstances. Finally, charcoal (carbon) burns in sulphur gas as it does in oxygen, but requires a higher temperature. The compound produced, carbon disulphide, has a similar composition to the oxygen compound, carbonic anhydride.

All those metals which combine with oxygen either at the ordinary temperature or when heated burn almost as easily in sulphur gas, forming sulphides, with a similar composition to the corresponding oxides. Thin copper foil brought into the vapour of boiling sulphur burns brilliantly, with a considerable evolution of light and heat, to form molten copper sulphide.

The sulphides of those metals of which the oxides are decomposed by heating—*e.g.* of silver, gold, platinum—are also reduced when heated, especially if exposed to the air. Mercuric sulphide (cinnabar), which simply volatilizes when heated, forms an exception to this rule, since the corresponding oxide is decomposed into mercury and oxygen by heat.

Accordingly as the oxides of the metals are soluble or insoluble in water, so are the corresponding sulphides. Soluble potassium sulphydrate corresponds to soluble potassium hydrate, calcium sulphide to calcium oxide, and insoluble lead sulphide to insoluble lead oxide.

The metallic sulphides which are soluble in water possess the property of uniting chemically with more atoms of sulphur than are contained in the normal compounds. Potassium sulphide (K_2S), for example, can unite with four more atoms of sulphur, producing potassium pentasulphide, which is also soluble in water :—

$$K_2S \ + \ 4S \ = \ K_2S_5.$$

If a solution of this or a similar polysulphide, soluble in water, is mixed with hydrochloric acid, the corresponding chloride is formed, sulphuretted hydrogen is liberated, and the excess of sulphur separates out as a fine, white, amorphous powder. *Milk of sulphur* is this *white* precipitate which has been washed and dried. The equation illustrating its production is as follows :—

$$K_2S_5 \ + \ 2HCl \ = \ 2KCl \ + \ H_2S \ + \ 4S.$$

SULPHURETTED HYDROGEN.

Composition : H_2S.

This compound is analogous to water in its composition, and also resembles water in many of its chemical properties. It is a colourless gas with a disgusting odour resembling rotten eggs, has a specific gravity of 1·19, and may be condensed, under pressure, to a mobile liquid, which solidifies at about $-85°$. The gas is somewhat soluble in water, to which it imparts its odour; the aqueous solution reacting slightly acid with litmus paper. A saturated solution in water at the ordinary temperature contains about three times its volume of the gas. Alcohol dissolves more, up to five times its volume.

Sulphuretted hydrogen, when inhaled in considerable quantities, is poisonous. The chemist, to whom the gas is indispensable, becomes more sensitive to the poison the more frequently it is inhaled, and the same is also true of other poisons, such as hydrocyanic (prussic) acid. In a high state of dilution, sulphuretted

hydrogen is present in many mineral waters—the so-called sulphureous springs (*e.g.* those of Aix-la-Chapelle, Harrogate). These waters are often used for medicinal purposes.

Sulphur and hydrogen unite directly with one another when hydrogen is led over heated sulphur; but as the affinity between the two substances is small, only a small quantity of the compound is produced. It is better to bring hydrogen in the nascent state into contact with sulphur, as by decomposing a suitable metallic sulphide with a strong acid.

The gas is easily obtained in quantity when pieces of ferrous sulphide contained in a Woulff's bottle are acted upon by dilute sulphuric or hydrochloric acid. In order to free the gas from mechanical impurities it is led through a wash-bottle containing water, and is then passed through a calcium chloride tube to dry it. It cannot well be collected over mercury, as it is partially decomposed by the metal, forming mercuric sulphide. It is best to employ warm boiled water, which dissolves much less of the gas than water at the ordinary temperature.

The ferrous sulphide used for the preparation of sulphuretted hydrogen usually contains some free iron, and the gas is therefore generally mixed with a small quantity of free hydrogen. In most cases this is immaterial, but if the gas is wanted quite pure it may be obtained by acting on antimonous sulphide (black antimony) with dry hydrochloric acid gas. The reactions in each of these cases are expressed in the following equations:—

$$\underset{\text{Ferrous sulphide}}{FeS} + 2HCl = H_2S + \underset{\text{Ferrous chloride}}{FeCl_2}.$$

$$\underset{\text{Antimonous sulphide}}{Sb_2S_3} + 6HCl = 3H_2S + \underset{\text{Antimonous chloride}}{2SbCl_3}.$$

Sulphuretted hydrogen is combustible, and is easily ignited. If a burning body is brought near a jet of the gas it catches fire and burns with a pale, bluish flame, producing water and sulphurous anhydride. If the supply of oxygen is insufficient, the hydrogen only burns, and yellow sulphur is separated. The combustion is always accompanied with the separation of sulphur, and it is therefore probable that the gas is first decomposed and its constituents afterwards burnt.

In fact the two elements in sulphuretted hydrogen are only very loosely combined. The compound is not only decomposed

by a high temperature, but also by all oxidizing agents, even the weakest, sulphur, being usually separated. Even the oxygen of the atmosphere decomposes it in presence of moisture. In a bottle half filled with sulphuretted hydrogen water, especially when often opened, the odour of the gas gradually disappears and the liquid becomes milky from separated sulphur. Sulphuretted hydrogen led through water containing iodine in suspension is rapidly decomposed, sulphur being set free and hydriodic acid formed; and this reaction may be utilized to prepare a dilute aqueous solution of hydriodic acid. Bromine and chlorine act in the same manner, but more energetically. Finally, ferric chloride is reduced by sulphuretted hydrogen to ferrous chloride with the formation of hydrochloric acid and the separation of sulphur:—

$$\underset{\text{Ferric chloride}}{Fe_2Cl_6} + H_2S = 2HCl + \underset{\text{Ferrous chloride}}{2FeCl_2} + S.$$

The insolubility of the majority of the metallic sulphides in water and the insolubility of some of them in dilute acids makes sulphuretted hydrogen a valuable reagent for the precipitation of many of the metals from the solutions of their salts. If the gas is led through a solution of silver nitrate, or if sulphuretted hydrogen water is added to this solution, a black precipitate of silver sulphide is formed and the solution then contains dilute nitric acid:—

$$2NO_2 \cdot OAg + H_2S = Ag_2S + 2NO_2 \cdot OH.$$

In the same manner the gas produces a yellow precipitate of arsenious sulphide in an acid solution of arsenious acid, an orange coloured precipitate of antimonous sulphide in a solution of antimonous chloride, &c.

The affinity of sulphur for most of the metals is so strong and for hydrogen so weak that some metals which do not combine directly with oxygen can decompose sulphuretted hydrogen. Silver, for example, becomes brown in an atmosphere containing the compound, owing to the production of silver sulphide. We say the silver tarnishes. This action is even produced by the minute quantities of the gas exhaled by the human body, contained in our coal-gas, and, therefore, always present in inhabited places. The darkening of oil paintings by age is also produced by the action of sulphuretted hydrogen. The lighter tints in these pictures nearly always contain white-lead (lead carbonate), and this becomes gradually converted into black lead sulphide.

HYDROGEN PERSULPHIDE

The composition of this body, which is richer in sulphur than sulphuretted hydrogen, has not yet been determined with certainty owing to its instability. Its probable composition is H_2S_2, corresponding to hydrogen peroxide, H_2O_2.

If hydrochloric acid is added to a solution of potassium pentasulphide, decomposition into potassium chloride, sulphuretted hydrogen, and sulphur occurs, as shown on page 145. But if the solution of potassium pentasulphide is poured into concentrated hydrochloric acid, there is produced, besides the substances mentioned above, a heavy oily liquid, with a piercing odour, which sinks to the bottom of the acid liquid. If this liquid is removed by a separating funnel and left to itself, it gradually decomposes into sulphuretted hydrogen and sulphur.

If the freshly-prepared oil is removed to a thick glass tube and then sealed up it undergoes the same decomposition. And the greater the quantity of sulphuretted hydrogen set free the greater becomes the pressure until finally the gas is liquefied. The sulphur which is set free at the same time is usually deposited as distinct crystals in the tube. Such tubes containing liquid sulphuretted hydrogen are dangerous to handle. It sometimes happens that they suddenly explode after having withstood the pressure of the gas for years.

OXIDES AND OXY-ACIDS OF SULPHUR.

Sulphur and oxygen unite together in two proportions and produce :—

Sulphurous anhydride . . . SO_2.
Sulphuric anhydride . . . SO_3.

In the former of these sulphur is a tetrad, in the latter it is a hexad. Both substances unite with bases and form stable salts, and the latter when combined with water yields the most important of the acids of sulphur :—

Sulphuric acid . . . $SO_2\begin{cases}OH\\OH\end{cases}$

Besides these compounds, which are by far the most important, a number of other oxy-acids of sulphur are known, partly in the free state and partly combined in their salts. They are all dibasic. Amongst the most important are :—

Thiosulphuric acid	$SO_2\begin{cases}OH\\SH\end{cases}$
Dithionic acid	$\begin{cases}SO_2\cdot OH\\SO_2\cdot OH\end{cases}$
Disulphuric acid	$O\begin{cases}SO_2\cdot OH\\SO_2\cdot OH\end{cases}$

Thiosulphuric acid is a derivative of sulphuric acid; in it one of the atoms of oxygen united with the hydrogen in sulphuric acid is displaced by an atom of diad sulphur. The two sulphur atoms in this compound have, therefore, different functions; the one atom is hexad, and the other, displacing the oxygen, is diad. Dithionic acid is a compound of two atoms of the monad radical $SO_2\cdot OH$; and in disulphuric acid two atoms of the same radical are united together by an atom of oxygen.

Besides these compounds the following are also known, although less thoroughly investigated :—

Hydrosulphurous acid . . .	$\begin{cases}SO\cdot OR\\SO\cdot OR\end{cases}$
Trithionic acid	$S\begin{cases}SO_2\cdot OR\\SO_2\cdot OR\end{cases}$
Tetrathionic acid . . .	$S_2\begin{cases}SO_2\cdot OR\\SO_2\cdot OR\end{cases}$
Pentathionic acid	$S_3\begin{cases}SO_2\cdot OR\\SO_2\cdot OR\end{cases}$

In these formulæ R stands for an atom of a monad metal in the salts of these acids, many of which have not been prepared in the free state.

Hydrosulphurous acid probably contains two atoms of tetrad sulphur each united with one atom of oxygen and with each other to form the diad radical $\begin{cases}SO\\SO\end{cases}$.

Tri-, tetra-, and pentathionic acids are probably similar in constitution to dithionic and disulphuric acids, and contain two atoms of the radical $SO_2\cdot OH$ united together by one, two, or three atoms of diad sulphur respectively.

SULPHUROUS ANHYDRIDE[1]

Composition: SO_2.

This compound, which is produced when sulphur burns in the air or oxygen, is a colourless gas with a powerful piercing odour, an acid reaction and taste. Its specific gravity is 2·216, and it contains its own volume of oxygen; for if sulphur is burnt in a closed volume of oxygen, the volume of the gas remains unchanged.[1] From these data the composition of the gas may be easily calculated, thus:—

2 vols. (1 molecule) sulphurous anhydride	weigh	$2·216 \times 28·88$	$= 64$
2 " " oxygen	"	2×16	$= 32$
1 atom of sulphur			32

—*i.e.* a molecule of sulphurous anhydride contains one atom of sulphur and two atoms of oxygen.

Sulphurous anhydride may be easily condensed by cold or pressure to a colourless mobile liquid, which boils at $-10°$ and solidifies under $-70°$.

The gas is absorbed by water in considerable quantities. One volume of water at the ordinary temperature absorbs about fifty times its volume of the gas. The aqueous solution possesses the odour of the gas and again gives it up when heated.

Sulphurous anhydride is contained in the gases of volcanoes. It is obtained in large quantities for technical purposes by burning sulphur or by roasting sulphurous ores (*e.g.* iron pyrites). The gas so obtained is of course very impure; it contains all the nitrogen present in the air employed.

The pure compound is best obtained by reducing sulphuric acid with some suitable metal—usually copper. Pieces of copper are placed in a large flask, covered with concentrated sulphuric acid, and the mixture gently heated until the evolution of gas begins (fig. 46). The two substances do not act upon one another in the cold. The gas is purified by passing it through a wash-bottle containing concentrated sulphuric acid, and is then collected in suitable vessels. As it is absorbed in such large quantities by water it cannot well be collected over this liquid; mercury may, however, be employed. It can also be easily collected by displacement by leading the gas to the bottom of the vessel to be filled

[1] See Appendix.

and loosely closing the mouth. The heavy gas gradually fills the jar and expels the lighter air before it.

Liquid sulphurous anhydride may be easily obtained in quantity by leading the pure gas into a tube surrounded with a freezing mixture of ice and salt; the tube (as shown in the figure) being contracted at one point so that it may be easily melted and hermetically sealed after a sufficient quantity of the gas has been condensed.

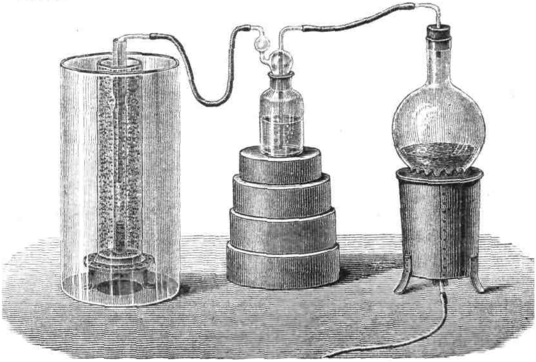


Fig. 46.

The production of sulphurous anhydride from sulphuric acid and copper may be expressed by the following equations, which indicate that an atom of copper first abstracts an atom of oxygen from the sulphuric acid, forming sulphurous acid and copper oxide, the former breaking up immediately into sulphurous anhydride and water, and the latter uniting with the excess of sulphuric acid to form copper sulphate and water :—

$$SO_2\begin{cases}OH\\OH\end{cases} + Cu = SO_2 + H_2O + CuO.$$

$$SO_2\begin{cases}OH\\OH\end{cases} + CuO = SO_2 \cdot O_2Cu + H_2O.$$

The final products are therefore sulphurous anhydride, copper sulphate, and water, and the whole reaction may be thus expressed :—

$$2SO_2\begin{cases}OH\\OH\end{cases} + Cu = SO_2 + SO_2\cdot O_2Cu + 2H_2O.$$

The student will notice that this process is essentially different from that which takes place when dilute sulphuric acid acts upon zinc to form zinc sulphate and hydrogen. In the latter case the two atoms of hydrogen in sulphuric acid are simply displaced by the equivalent quantity of zinc (one atom) :—

$$SO_2\begin{cases}OH\\OH\end{cases} + Zn = SO_2\cdot O_2Zn + H_2;$$

while in the former case the sulphuric acid loses an atom of oxygen and becomes reduced to sulphurous acid.

Only a few metals besides copper can reduce sulphuric acid in this manner; among them are mercury and silver.

Sulphurous anhydride mixed with carbonic oxide and carbonic acid may also be cheaply obtained in large quantities by heating concentrated sulphuric acid with charcoal :—

$$SO_2\begin{cases}OH\\OH\end{cases} + C = SO_2 + CO + H_2O.$$

This method is valuable for those purposes where the admixture with carbonic oxide and acid has no injurious effect—for example, in the manufacture of the sulphites.

Sulphurous anhydride is a compound radical called *sulphuryl*, and behaves in its compounds like a diad element. Mixed with oxygen and led over heated platinum in a finely divided state the two substances unite to form sulphuric anhydride :—

$$SO_2 + O = SO_3.$$

Its aqueous solution absorbs oxygen from the air and becomes converted into sulphuric acid. It further unites directly with chlorine, when a mixture of the gases is exposed to bright sunlight, producing *sulphuryl chloride*—SO_2Cl_2. This compound is a colourless liquid with a powerful odour, which boils at 70° and is decomposed by water into hydrochloric and sulphuric acids.

From a saturated solution of the gas in water at 0° a crystalline compound separates out, having the composition $SO_2 + 15H_2O$. It melts at 4°, and is decomposed into its constituents.

Most bodies which easily give off oxygen oxidize sulphurous anhydride, in the presence of water, to sulphuric acid. It is absorbed by manganese peroxide forming manganous sulphate and by lead peroxide producing lead sulphate :—

$$SO_2 + PbO_2 = SO_2\cdot O_2Pb.$$

The production of this lead sulphate is accompanied with a large evolution of light and heat. If a little dried lead peroxide enclosed in a piece of thin muslin is brought into a jar of the dry gas, the black oxide becomes red-hot and is rapidly converted into white lead sulphate.

Under ordinary circumstances hydrogen has no action on sulphurous anhydride, but in the nascent state, especially in the presence of acids, the latter is reduced to sulphuretted hydrogen and sulphur. If a little of the aqueous solution is poured into a flask containing zinc and sulphuric acid, the hydrogen which is evolved soon smells strongly of sulphuretted hydrogen and produces a black precipitate of lead sulphide if led into a solution of lead acetate, at the same time the liquid in the flask becomes milky from separated sulphur. The sulphur which is here set free is produced by the action of sulphuretted hydrogen upon sulphurous anhydride. Whenever these two substances come into contact with one another, whether in the gaseous state or in solution in water, mutual decomposition ensues into sulphur and water :—

$$2H_2S + SO_2 = 2H_2O + 3S.$$

When the reaction takes place slowly the sulphur is often deposited in the crystalline form, and it is possible that considerable quantities of the sulphur occurring free in nature have been produced by this reaction.

Sulphurous anhydride bleaches organic colouring matters like chlorine, but the bleaching effect is produced in a different way. We have seen that chlorine bleaches partly by the formation of colourless substitution compounds, and partly by oxidation in the presence of water, or by both processes together, and the bleached colours cannot be therefore restored. But it appears as if the bleaching of sulphurous anhydride were produced by its direct union with the colouring substances. And as sulphurous anhydride can be expelled from its compounds by strong acids, the colour of many bodies bleached with this substance may be restored by treatment with strong acids. A rose which has been bleached by sulphurous anhydride regains its colour when washed with water and placed in dilute sulphuric acid. Similarly, a substance which unites with sulphurous anhydride more powerfully than the colouring matter (*e.g.* a strong base), will also restore the colour. Flannel which has been repeatedly washed regains the original yellow colour of the wool owing to the action of the alkali contained in the

soap used in cleansing it. Substances upon which chlorine acts too energetically—silk, wool, straw, &c.—are usually bleached by sulphurous anydride.

Sulphurous anhydride also possesses powerful antiseptic properties. It destroys the smell of decomposing organic substances and stops the action of those organisms which produce fermentation and putrefaction. Burning sulphur was used as early as Homer's time to disinfect closed spaces.[1]

Sulphurous acid—probably $SO\left\{\begin{matrix}OH\\OH\end{matrix}\right.$—is known only in the *sulphites*. It is a weak dibasic acid, and forms, therefore, two series of salts, normal and acid—*e.g.* :—

Normal sodium sulphite	$SO\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.$
Acid sodium sulphite	$SO\left\{\begin{matrix}OH\\ONa\end{matrix}\right.$

The sulphites are formed by the union of sulphurous anhydride with strong bases. They are all decomposed by dilute mineral acids, with liberation of sulphurous anhydride.

The presence of sulphurous acid in any of its compounds may be detected by the odour of the gas when liberated by a dilute acid. If the quantity is too small to be detected in this way, the gas may be allowed to act upon iodic acid, when sulphuric acid and free iodine are produced. If a piece of paper moistened with a solution of iodic acid and a little starch is hung up in a cylinder containing the liquid to be examined, the paper soon becomes blue, owing to the union of the liberated iodine with the starch.

The sulphites may, however, have a different composition to that given above. They may be formed on the type of the hypothetical acid $SO_2\left\{\begin{matrix}OH\\H\end{matrix}\right.$, which would be called hydrosulphuric acid. This acid would then be a monobasic acid, but in which the second atom of hydrogen—that united directly to the sulphur—could also be displaced by a metal. What we now call acid sodium sulphat

[1] 'Bring sulphur straight and fire' (the monarch cries);
She hears, and at his word obedient flies.
With fire and sulphur, cure of noxious fumes,
He purg'd the walls and blood-polluted rooms.
Odyssey, xxii. 527–530. (Pope's *Translation*.)

would then be the normal hydrosulphate : $SO_2\begin{cases}ONa\\H\end{cases}$, and our normal sulphite would be sodium sodiosulphate : $SO_2\begin{cases}ONa\\Na\end{cases}$. These considerations are supported by many facts in organic chemistry, and the decision which view is correct cannot be long delayed. Possibly isomeric salts of the two acids exist together.

Hyposulphurous acid: $\begin{cases}SO\cdot OH\\SO\cdot OH\end{cases}$, has not yet been obtained in the pure state. An impure solution is prepared by digesting a concentrated aqueous solution of sulphurous anhydride with metallic zinc. The yellow liquid so obtained, which contains hyposulphurous acid, possesses powerful reducing and bleaching properties. It rapidly decomposes first into thiosulphuric acid and then into sulphurous anhydride, water, and sulphur. The sodium salt may be prepared by digesting together zinc and a solution of acid sodium sulphite. Schützenberger, the discoverer of this acid, gave it a composition which has been recently proved to be incorrect. He supposed it to be a monobasic acid, represented by the formula $SO\begin{cases}OH\\H\end{cases}$; but we now know that the acid is dibasic, its correct formula being that given above.[1]

SULPHURIC ACID.

Composition: H_2SO_4, or $SO_2\begin{cases}OH\\OH\end{cases}$

If a further atom of oxygen is made to unite with sulphurous anhydride, the compound sulphuric anhydride (SO_3) is formed. But far more important than this body is the substance produced when it unites with water—viz. sulphuric acid, or *oil of vitriol*, as it is sometimes called from the old method of preparing it.

Sulphuric acid is a compound of hexad sulphur, and contains the radical SO_2 united to two atoms of hydrogen through the intervention of two oxygen atoms.

Sulphuric acid is a colourless, odourless, viscid liquid, which does not fume in the air, and has a specific gravity of 1·84. It boils

[1] See Appendix.

at 338° and can be distilled, but only with partial decomposition, into sulphuric anhydride and water. It mixes with water in all proportions, and during mixing evolves a large quantity of heat. Even when very largely diluted with water it reacts and tastes strongly acid. Below 0° it freezes to a crystalline solid.

In nature sulphuric acid occurs chiefly in combination with lime as *gypsum* or *anhydrite*, widely distributed and in very large quantities, and besides this as *heavy spar* or *barite* (barium sulphate), as *celestine* (strontium sulphate), as *Glauber's salt* (sodium sulphate), &c.

Calcium sulphate is such a common mineral that it might be thought capable of yielding an inexhaustible source of cheap sulphuric acid, and this would be so were it possible to separate the sulphuric acid from its combination with the lime as easily as we can separate carbonic acid from chalk or nitric acid from nitre. But sulphuric acid is so firmly united with the lime in calcium sulphate that we can neither expel it by heating nor by the action of a stronger acid, and gypsum is not therefore adapted for the manufacture of sulphuric acid, nor has it ever been used for this purpose.

The acid may, however, be obtained in many other ways. Sulphur, which burns in oxygen to sulphurous anhydride, is converted when heated with concentrated nitric acid or other powerful oxidizing agents into the higher oxide—sulphuric acid And here the question may present itself, Why is it that while carbon and phosphorus when burning in the air always produce their higher oxide, sulphur only forms its lower oxide? The reason is that sulphuric anhydride cannot exist at a high temperature, but is decomposed into oxygen and its lower oxide, and that the temperature of combustion of sulphur is higher than the point at which sulphuric anhydride is decomposed. If we could by any means lower the temperature of combustion of sulphur, it would undoubtedly produce sulphuric anhydride when burning in air, but up to the present this problem has not been solved, and we must therefore look for some other method of oxidation. The best substance for this purpose, and that exclusively used for the manufacture of sulphuric acid, is nitric acid.

In order to understand this process, it must be remembered that nitric acid, which has the composition $NO_2 \cdot OH$, yields up a portion of its oxygen and becomes converted into nitric oxide (NO) in the presence of sulphurous anhydride and water. Three molecules of sulphurous anhydride therefore require two

molecules of nitric acid and two of water to be converted into sulphuric acid :—

$$3SO_2 + 2NO_2{\cdot}OH + 2H_2O = 3SO_2\begin{cases}OH\\OH\end{cases} + 2NO.$$

But if as in this equation two molecules of nitric acid were consumed in the production of every three molecules of sulphuric acid, the price of the latter acid would be scarcely lower than that of the former. As a matter of fact, the nitric acid can oxidize much larger quantities of sulphurous acid than that expressed in the above equation—more than ten times as much. This is rendered possible by the remarkable property which the colourless nitric oxide possesses of uniting with the oxygen of the air, even at the ordinary temperature, and forming red vapours consisting of nitrous anhydride and nitric peroxide, and these gases again give up oxygen to sulphurous anhydride, oxidizing it to sulphuric acid in the presence of water, and being themselves again reduced to nitric oxide. It thus appears as if a small quantity of nitric oxide would be able to convert an unlimited quantity of sulphurous anhydride into sulphuric acid, if allowed to act upon a mixture of the gas and pure oxygen together with water vapour in the correct proportions. The oxygen would at once convert the nitric oxide (NO) into nitric peroxide (NO_2), which would be again reduced to nitric oxide in the presence of sulphurous anhydride and water vapour :—

$$NO_2 + SO_2 + H_2O = SO_2\begin{cases}OH\\OH\end{cases} + NO,$$

and this could then produce further quantities of sulphuric acid, and so on. (See Appendix.)

But such a process cannot be carried on in practice, simply becauses it presupposes an inexhaustible supply of pure oxygen. The manufacturer must make use of the oxygen contained in the air. The air, by the gradual abstraction of its oxygen, becomes largely diluted with nitrogen, and ultimately the small proportion of oxygen present will not unite with the nitric oxide sufficiently quickly. When this point is reached, the valuable nitrogen compounds would be wasted if a method had not been discovered of condensing them, and reintroducing them into the chambers.

The manufacture of sulphuric acid on a large scale, based upon the above-mentioned chemical principles, is conducted as follows.

The sulphurous anhydride is obtained either by burning sulphur

or by roasting iron pyrites. It is then allowed to stream, mixed with atmospheric air, into a large leaden chamber, where it comes into contact with nitric acid vapours. A small portion of the sulphurous anhydride is at once oxidized by the nitric acid to sulphuric acid, but by far the greater portion passes on, mixed with nitric peroxide, nitrous anhydride, and nitric oxide, into the next chamber, into which steam is led from a boiler. The reactions mentioned above go on in this chamber, and the dilute sulphuric acid collects on the floor.[1]

The motion of the gases through the chambers is produced by a tall shaft placed at the further end, which returns the useless nitrogen to the atmosphere. But before it reaches the shaft it is made to pass through what is called a Gay Lussac's tower to retain the valuable oxides of nitrogen so that they may be again used to produce a further quantity of sulphuric acid. It has been found that strong sulphuric acid can absorb nitric peroxide, and especially nitrous anhydride, in considerable quantities. This property is utilized in the Gay-Lussac's tower by causing strong sulphuric acid to trickle down in a finely divided state over pieces of coke, in order to expose as large a surface of the acid as possible to the ascending gases. The strong acid containing the oxides of nitrogen in solution (so-called *nitrated acid*), which collects at the foot of the tower, is pumped back to the other end of the chambers. The gases which it contains are then again liberated by mixing it with dilute acid, and are again introduced into the chambers by allowing it to flow down a second tower (Glover's tower), through which the sulphurous anhydride and air are made to pass.

The chambers in which the sulphuric acid is produced are made of lead, because lead is the only substance available which resists to some extent the action of sulphuric acid. The leaden plates constituting the chambers are melted together by means of the oxy-hydrogen blowpipe, and are supported externally by a stout wooden framework.

The acid which collects on the floor of the chambers—the *chamber acid*—is somewhat dilute, and only contains little more

[1] The reactions given here only explain in a general manner what goes on in the chambers. What really happens is doubtful, and is probably dependent upon the proportions in which the various substances are introduced into the chambers. If the supply of steam is deficient, white crystals having the composition $SO_2\begin{cases}OH\\NO_2\end{cases}$ are produced, which under the action of water at once break up into sulphuric acid, nitric acid, and nitric oxide.—ED.

than 64 per cent. of the pure acid (sp. gr. = 1·55). By heating in leaden vessels it is concentrated until it contains about 78 per cent. of the pure acid. This is the *brown acid* of commerce, and has a specific gravity of about 1·71. The concentration cannot be carried further in leaden vessels, as at this point the lead begins to be attacked. Further concentration is then carried on in vessels of glass or better of platinum. The sulphuric acid so prepared is usually coloured brown from traces of organic substances, and always contains lead sulphate in solution. If diluted with water or alcohol, the liquid becomes turbid, and ultimately deposits a white precipitate of this lead sulphate, which is more soluble in the concentrated than in the dilute acid.

If iron pyrites is used in the manufacture of sulphuric acid, the acid always contains arsenic, sometimes in not inconsiderable quantities. A sample of the acid containing arsenic when diluted with water, and saturated with sulphuretted hydrogen, first turns yellow, and then deposits a yellow precipitate of arsenious sulphide. By far the greater quantity of sulphuric acid which is brought into trade contains arsenic; only a comparatively small quantity of the more expensive acid free from arsenic is manufactured from Sicilian sulphur.

The colourless, concentrated, chemically pure sulphuric acid is prepared by distilling the acid free from arsenic in platinum vessels. During distillation it always undergoes a partial decomposition into sulphuric anhydride, which passes over with the distillate and water which remains behind; this goes on until the acid contains 98 per cent. of the pure compound, which then distils over unchanged. (See Appendix.)

Sulphuric acid is one of the strongest acids, and expels therefore nearly every other acid from its compounds. It is, like sulphurous acid, a dibasic acid, and its acid salts possess a strong acid reaction and taste. With few exceptions, its salts are soluble in water. Sulphuric acid is distinguished by its powerful attraction for water, with which it unites in several definite proportions, always evolving a large quantity of heat. The compound with one molecule of water—$SO_2\begin{cases}OH\\OH\end{cases} + H_2O$ — has the specific gravity 1·78, and solidifies in a crystalline form at + 8°. Unlike water, it does not expand on solidification, and vessels filled with this acid do not therefore burst on freezing If to this compound a further

quantity of water is added, a further quantity of heat, though less than before, is evolved. And the quantities of heat which are set free when one, two, or three molecules of water unite with one molecule of sulphuric acid are in a certain definite proportion to one another.

The strong attraction of sulphuric acid for water is employed to dry those gases upon which the acid has no action (*e.g.* oxygen, hydrogen, carbonic acid), the gases being simply led through a wash-bottle containing the strong acid. It also serves to dry solid and liquid bodies which are placed in a closed space (a desiccator) with the concentrated acid. The acid then rapidly absorbs all the water vapour which evaporates from the substances to be dried.

Ordinary commercial sulphuric acid is always of a brownish colour, due to the decomposition of particles of dust of organic origin. If a splinter of wood is dipped into the concentrated acid it soon becomes brown and then black from the charcoal which the acid has set free from the wood by abstracting oxygen and hydrogen in the form of water. These elements are not present as water in the wood, but the acid compels them to combine to form water, with which it then unites.

Sulphuric acid is by no means so permanent as its powerful affinities and high boiling point might lead us to suppose. Even below a red heat, if allowed to drop upon hot bricks or upon pieces of pumice stone contained in a hot platinum retort, it is decomposed into water, oxygen, and sulphurous anhydride. If the mixture of gases so obtained is led into a solution of caustic soda, the sulphurous anhydride is absorbed, and considerable quantities of pure oxygen may be obtained. The instability of sulphuric acid at high temperatures is the reason why burning sulphur produces sulphurous anhydride and not sulphuric anhydride.

Nascent hydrogen reduces concentrated sulphuric acid (not the dilute acid) to sulphuretted hydrogen :—

$$SO_2\begin{cases}OH\\OH\end{cases} + 4H_2 = H_2S + 4H_2O.$$

If a few drops of concentrated sulphuric acid are allowed to flow by means of a funnel tube into a flask evolving hydrogen, the hydrogen soon acquires the characteristic odour of sulphuretted hydrogen, and produces a black precipitate of lead sulphide in a solution of lead acetate. Zinc, iron, nickel, manganese, and other metals which possess a strong attraction for oxygen and are

dissolved by dilute sulphuric acid with evolution of hydrogen, are not attacked even when heated with the concentrated acid, probably because their sulphates are so insoluble in the concentrated acid that they incrust the metals and prevent any further action. Other metals, as copper and mercury, which in consequence of a feebler attraction for oxygen are not attacked by dilute sulphuric acid, reduce the concentrated acid when heated with it, forming sulphurous anhydride and a sulphate soluble in concentrated sulphuric acid. In this way sulphuric acid, which we prepare from impure sulphurous anhydride, affords us the best material for the preparation of this substance in the pure state.

Sulphuric acid contains two atoms of displaceable hydrogen, and is therefore a dibasic acid. With monad metals it forms two series of salts—the normal and acid—*e.g.* :—

Normal sodium sulphate . . . . $SO_2\begin{cases} ONa \\ ONa \end{cases}$

Acid sodium sulphate . . . . $SO_2\begin{cases} OH \\ ONa \end{cases}$

Most of the *sulphates* are soluble in water, the most important exception being barium sulphate, which is quite insoluble in water and dilute acids, and which is therefore used to detect sulphuric acid or a sulphate in an aqueous solution. On the addition of a few drops of barium chloride to such a solution, the presence of sulphuric acid is at once recognized by a white turbidity or precipitate of barium sulphate which is insoluble in hydrochloric acid.

The great progress which has been made during the past fifty years in technical chemistry and the arts generally, is due to a large extent to improvements in the manufacture of sulphuric acid. Hundreds of thousands of tons of sulphuric acid are manufactured annually in England, Germany, and France alone, and by far the greatest part of this immense quantity is used for the production of soda, from which again two of the most indispensable articles of daily life—soap and glass—are obtained. Besides this the acid is also used for an immense number of other chemical processes, and, in fact, there is scarcely any chemical manufacture in which sulphuric acid does not take a direct or indirect part. It will, therefore, be at once apparent that a reduction in the price of this important substance to one-tenth the amount paid for it a little more than a century ago must have exercised a most beneficial influence on the development of technical chemistry.

If, as is not only possible but even probable, further improve-

ments are made in the manufacture of sulphuric acid, and its price becomes still lower, the price of soda, glass, soap, and stearine, of superphosphate manures and hundreds of other things, would at once fall to a considerable extent.

SULPHURIC ANHYDRIDE.

Composition : SO_3.

This substance, which is sometimes called sulphuric acid, is very unlike sulphuric acid in its properties. It is a solid body, crystallizing in white, silky needles. It melts at 15° and boils at 46°, producing vapours which form thick white fumes of sulphuric acid in moist air. The density of its vapour, compared with the air as unity, is 2·77, corresponding to a molecular weight of 80.

Sulphuric anhydride may be easily obtained from sulphurous anhydride and oxygen. A mixture of the two gases remains unchanged even if heated or exposed to sunlight, but if led over a layer of heated platinum, contained in a tube of hard glass, the two substances at once unite with one another, and the presence of sulphuric anhydride is made manifest by the dense white fumes produced where the gases come into contact with the air. The platinum itself remains quite unchanged; it acts in some unknown manner upon the gaseous mixture, and its action is an example of what is called, for want of a better name, *contact action*. Perhaps the phenomenon depends upon the property of platinum to condense considerable quantities of oxygen on its surface and so liquefy the gas; or it may be that the oxygen is converted into its active modification—ozone. Instead of pure platinum it is better to employ platinized asbestos—*i.e.* asbestos of which the surface has been covered with a thin layer of platinum.[1]

Sulphuric anhydride is commonly prepared from Nordhausen or fuming sulphuric acid, which may be considered as a solution of the anhydride in sulphuric acid. When this acid is gently heated in a retort, the anhydride volatilizes and condenses in a cool dry receiver as a colourless crystalline mass.

Sulphuric anhydride is especially characterized by its strong attraction for water. If a drop of the molten substance is allowed

[1] Prepared by dipping asbestos into platinic chloride solution, drying, and heating to redness.—Ed.

to fall into a vessel of water, it sets free a large quantity of heat and hisses like a red-hot iron on immersion in water. If a drop of water happens to fall into a glass vessel containing the anhydride, chemical union at once takes place with an explosion, and the vessel is always shattered. In all cases the compound produced by its union with water is sulphuric acid. Sulphuric anhydride acts even more powerfully on organic substances than sulphuric acid; it abstracts water and chars them. A cork or india-rubber stopper cannot, therefore, be used to close a bottle containing the volatile anhydride. Formerly sulphuric anhydride was only employed for certain reactions in the laboratory on a small scale, but it is now used more and more in the arts; for example, in the manufacture of alizarine from anthracene. It is now prepared in considerable quantities in chemical works, and is an article of commerce.

NORDHAUSEN OR FUMING SULPHURIC ACID.

This acid is not a definite chemical compound, but consists (as we have previously stated) of sulphuric acid containing more or less sulphuric anhydride in solution. In former times it was principally manufactured at Nordhausen, in the Harz Mountains, though at present none is made there.

Fuming sulphuric acid is a thick oily liquid, usually coloured brown from the presence of minute particles of carbon, and is distinguished from ordinary sulphuric acid by the fact that it fumes in the air. These fumes consist of the volatile sulphuric anhydride which it gives off, and which unites with the moisture of the air.

The acid is usually prepared from green vitriol (ferrous sulphate). This salt crystallizes with seven molecules of water, and has the composition: $SO_2 \cdot O_2Fe + 7H_2O$. When heated in the air it easily loses six molecules of water, but the seventh only at a higher temperature, at which the salt itself begins to be decomposed. The salt, after being dried as thoroughly as possible, is heated in clay retorts provided with receivers of the same material. It is then decomposed into ferric oxide (called *caput mortuum* or *colcothar*), which remains behind in the retorts, and sulphurous anhydride with sulphuric anhydride, which distil over, the latter condensing in the cool receivers. The small quantity of water which the dried salt still contains suffices to convert the sulphuric anhy-

dride in the retort into liquid fuming sulphuric acid. The following equation represents the process :—

$$2SO_2 \cdot O_2Fe = Fe_2O_3 + SO_2 + SO_3.$$

A larger quantity of acid is obtained, and without the production of sulphurous anhydride, when the mother-liquor from ferrous sulphate, which contains the ferric salt, is evaporated and calcined. The mass so obtained consists principally of basic ferric sulphate of the composition: $S_2O_9Fe_2 = 2SO_3, Fe_2O_3$, which on further heating in retorts breaks up into ferric oxide and sulphuric anhydride.

As was stated on p. 162, fuming sulphuric acid when heated in a retort boils and gives off the sulphuric anhydride which it contains even below 100°. As the quantity of anhydride becomes less and less the boiling point rises, until at last ordinary sulphuric acid remains in the retort.

When cooled, fuming sulphuric acid deposits colourless crystals, which melt at 35°, and consist of disulphuric acid, the properties of which are described below (p. 166).

Sulphurous anhydride can unite not only with an atom of oxygen but also with an equivalent quantity—*i.e.* two atoms—of chlorine. The compound so produced is *Sulphuryl chloride*: SO_2Cl_2. Besides this body another chlorine compound is known, intermediate between sulphuryl chloride and sulphuric acid, and which may be considered as sulphuric acid with one atom of hydroxyl (OH) displaced by one atom of chlorine. This is *Chlorsulphonic acid*: $SO_2\begin{cases}Cl\\OH\end{cases}$. The latter is a monobasic acid, because it contains one atom of hydrogen displaceable by a metal, while the former is an indifferent substance, and cannot enter into combination with bases.

SULPHURYL CHLORIDE.

Composition: SO_2Cl_2.

This substance is a mobile colourless liquid, with a piercing odour. It fumes slightly in the air, has a specific gravity of 1·7, and boils at 70°. It may be obtained by direct union of chlorine and sulphurous anhydride when a mixture of the two gases in equal volumes is exposed to direct sunlight, or more readily, and in larger quantities, when chlorsulphonic acid is heated in closed

tubes to 200° or 210° for about twelve hours. Two molecules of chlorsulphonic acid are then decomposed into one molecule of sulphuryl chloride and one of sulphuric acid :—

$$2SO_2\begin{cases}Cl\\OH\end{cases} = SO_2Cl_2 + SO_2\begin{cases}OH\\OH\end{cases}$$

The liquid product, which is usually of a greenish yellow colour, is heated in a retort, and the portion passing over up to 110° again rectified on the water bath. The portion which then distils over at about 70° is nearly pure sulphuryl chloride. In order to separate minute quantities of chlorsulphonic acid and sulphuric anhydride, which it still contains, the distillate is poured into a separating funnel containing pieces of ice. The ice at once acts upon these impurities, while the sulphuryl chloride, which is scarcely attacked, sinks as a heavy oil to the bottom of the funnel. It is then freed from water with phosphoric anhydride, redistilled, and if the first portions of the distillate, which contain sulphurous acid and chlorine, are rejected, is so obtained perfectly pure.

Sulphuryl chloride is easily decomposed by water into sulphuric and hydrochloric acids :—

$$SO_2Cl_2 + 2H_2O = SO_2\begin{cases}OH\\OH\end{cases} + 2HCl.$$

CHLORSULPHONIC ACID.

Composition : $SO_2\begin{cases}Cl\\OH\end{cases}$

This substance is also a colourless liquid, with a specific gravity of 1·77, and boiling at 153°. It is at once decomposed by water, with a considerable evolution of heat, into sulphuric and hydrochloric acids :—

$$SO_2\begin{cases}Cl\\OH\end{cases} + H_2O = SO_2\begin{cases}OH\\OH\end{cases} + HCl.$$

Chlorsulphonic acid may be produced by the direct union of sulphuric anhydride and hydrochloric acid gas—$SO_2O + HCl = SO_2\begin{cases}Cl\\OH\end{cases}$, but is best obtained by heating together molecular weights of sulphuric acid and phosphorus pentachloride, when hydrochloric acid and phosphoric oxychloride are also produced :—

$$SO_2\begin{cases}OH\\OH\end{cases} + PCl_5 = SO_2\begin{cases}Cl\\OH\end{cases} + POCl_3 + HCl.$$

It may then be separated from the more volatile phosphoric oxychloride (B.P. = 110°) by fractional distillation. Metallic salts of chlorsulphonic acid have not yet been prepared.

NITROSULPHONIC ACID.

Composition: $SO_2\begin{cases}NO_2\\OH\end{cases}$

This compound, which may be considered as sulphuric acid in which one atom of hydroxyl is displaced by the group of atoms NO_2, separates out as colourless crystals when nitric peroxide is led into concentrated sulphuric acid or sulphurous anhydride into cold fuming nitric acid. The latter reaction is expressed by the equation:—

$$SO_2 + NO_2OH = SO_2\begin{cases}NO_2\\OH\end{cases}$$

Nitrosulphonic acid is also produced by the action of sulphurous anhydride on a mixture of nitric oxide and oxygen in the presence of a small quantity of water, and occurs therefore in the sulphuric acid chambers when the quantity of steam is insufficient. The so-called *white crystals* to which we have previously referred (p. 158 *note*), consist of this compound, and their presence in the chambers is usually considered to indicate irregularities in the manufacture.

Nitrosulphonic acid is dissolved by sulphuric acid, but decomposes when gently heated or when brought into contact with water. In the latter case sulphuric acid and nitrous acid are produced, and the latter then decomposes into nitric oxide and nitric acid. When dissolved in sulphuric acid it requires a greater quantity of water to decompose it than when in the free state.

DISULPHURIC ACID.

Composition: $H_2S_2O_7 = O\begin{cases}SO_2OH\\SO_2OH\end{cases}$

The latter formula indicates that two atoms of the sulphuric acid radical (sulphuryl = SO_2) are contained in a molecule of disulphuric acid, that they are united together by an atom of oxygen,

and that the other two unsatisfied bonds of the SO_2 are connected with two atoms of hydroxyl (HO), the hydrogen of which can be displaced by metals; the acid is therefore dibasic.

Disulphuric acid is deposited from fuming sulphuric acid at a low temperature as colourless and often large-sized crystals, which melt at 35° and fume in the air. It is decomposed when brought into contact with water into ordinary sulphuric acid :—

$$O\begin{cases} SO_2\cdot OH \\ SO_2\cdot OH \end{cases} + H_2O = 2SO_2\begin{cases} OH \\ OH \end{cases}$$

and when heated into sulphuric anhydride and sulphuric acid :—

$$O\begin{cases} SO_2\cdot OH \\ SO_2\cdot OH \end{cases} = SO_3 + SO_2\begin{cases} OH \\ OH \end{cases}$$

Its salts are more stable than the free acid. The sodium salt is easily obtained by heating acid sodium sulphate as long as water is expelled. The following equation shows the reaction :—

$$\underset{\text{Acid sodium sulphate}}{2SO_2\begin{cases} ONa \\ OH \end{cases}} = \underset{\text{Sodium disulphate}}{O\begin{cases} SO_2\cdot ONa \\ SO_2\cdot ONa \end{cases}} + H_2O.$$

This salt dissolves in water unchanged. When strongly heated it breaks up into normal sodium sulphate and sulphuric anhydride :—

$$O\begin{cases} SO_2\cdot ONa \\ SO_2\cdot ONa \end{cases} = SO_2\begin{cases} ONa \\ ONa \end{cases} + SO_3.$$

THIOSULPHURIC ACID.

Thiosulphuric acid is not known in the free state, but only in its salts. *It is a dibasic acid, and is to be considered as sulphuric acid,* in which one of the atoms of oxygen united with the hydrogen is displaced by diad sulphur. The *composition* of the hypothetical acid is therefore $SO_2\begin{cases} SH \\ OH \end{cases}$, or $H_2S_2O_3$. Before the relations of thiosulphuric acid to sulphuric acid were known, the acid was compared with dithionic acid, which has the empirical formula, $H_2S_2O_6$. Whence arose the former name for this acid: *hyposulphurous acid*,[1] based upon the old name for dithionic acid—hyposulphuric acid.

[1] This name survives in the commercial designation for the sodium salt: *hyposulphite of soda.*—ED.

Of the compounds of thiosulphuric acid we are only acquainted with its metallic salts, some of which are stable substances, and of which the sodium salt is most easily obtained in the crystalline state. If we endeavour to set free the thiosulphuric acid from its salts by means of a stronger acid, we find that the acid can only exist for a very short time even in dilute solutions. The liquid soon becomes turbid from deposited sulphur, and begins to smell of sulphurous anhydride. The acid decomposes in fact into sulphur, sulphurous anhydride, and water :—

$$SO_2\begin{cases}SH\\OH\end{cases} = SO_2 + S + H_2O.$$

This reaction may be used for the detection of the thiosulphates, especially as the separated sulphur always possesses a yellow colour. The best known salt is sodium thiosulphate, which with the potassium salt is distinguished by its stability. This important salt may be obtained in various ways. It is produced if an aqueous solution of neutral sodium sulphite is boiled with sulphur :—

$$SO\begin{cases}ONa\\ONa\end{cases} + S = SO_2\begin{cases}ONa\\SNa\end{cases}$$

or if sulphurous anhydride is led into a solution of sodium monosulphide. Normal sodium sulphite and sulphuretted hydrogen are then first produced :—

$$SO_2 + Na_2S + H_2O = SO\begin{cases}ONa\\ONa\end{cases} + H_2S,$$

and the latter gas reacts at once on the excess of sulphurous anhydride, forming water and free sulphur :—

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

The greater part of this sulphur sinks to the bottom of the vessel, but a portion unites with the sodium sulphite to form sodium thiosulphate.

Sulphur therefore acts on the sulphites in the same way as oxygen. Just as a solution of sodium sulphite when exposed to the air absorbs oxygen and becomes converted into sodium sulphate, so the same solution when warmed with powdered sulphur unites with it to form the corresponding thiosulphate. The composition of thiosulphuric acid is also interesting because its molecule contains two atoms of sulphur of different valency. The atom in the radical sulphuryl (SO_2) is hexad, while that uniting the atom of hydrogen or monad metal to this radical is diad. Sodium thiosul-

phate, together with polysulphides, is produced when a solution of caustic soda is boiled with an excess of sulphur :—

$$6NaOH + 12S = SO_2\begin{cases}ONa\\SNa\end{cases} + \underset{\text{Sodium pentasulphide}}{2Na_2S_5} + 3H_2O.$$

Finally, some sulphides (*e.g.* that of calcium) are oxidized when exposed to the air and converted into thiosulphates. Calcium sulphide is largely produced as a bye-product in the manufacture of soda, and this *alkali-waste* when exposed to the air becomes partly converted into calcium thiosulphate, which, when digested with a solution of sodium carbonate or sulphate, yields insoluble calcium carbonate or sulphate, and a solution of sodium thiosulphate.

The compounds of thiosulphuric acid with the heavy metals are mostly insoluble and easily decomposed. Sodium thiosulphate produces in a solution of silver nitrate a yellowish white precipitate of silver thiosulphate. This salt, however, rapidly darkens in colour, and at last becomes quite black, owing to the formation of silver sulphide and sulphuric acid :—

$$SO_2\begin{cases}OAg\\SAg\end{cases} + H_2O = Ag_2S + SO_2\begin{cases}OH\\OH\end{cases}$$

In the same way the white lead salt blackens on boiling, and for the same reason.

The extraordinary property which sodium thiosulphate, in common with other soluble thiosulphates, possesses of dissolving chloride, bromide, and iodide of silver, with which it forms soluble double salts, is of considerable importance. Use is made of this property chiefly in the production of photographs. After the sensitive plate, which is coated with a thin layer of these compounds, has been exposed in the camera, and after the iodide, &c., of silver has been decomposed in those parts on which the light has fallen, it becomes necessary in order to make the picture permanent to remove the iodide, &c., which has remained unchanged. This is effected by dipping the plate into a solution of sodium thiosulphate, which at once removes the unchanged compounds. Many tons of sodium thiosulphate are annually manufactured for this purpose.

DITHIONIC ACID.

This acid, formerly called *hyposulphuric acid*, has not been isolated, but is known in aqueous solution and in combination as salts. From the composition of these bodies we consider the acid to be :—

$$H_2S_2O_6 = \begin{cases} SO_2OH \\ SO_2OH \end{cases}$$

the latter formula expressing that the molecule of the acid consists of two atoms of the radical : SO_2OH, each of which contains an atom of displaceable hydrogen, thus making the acid dibasic.

Manganous dithionate may be obtained by leading sulphurous anhydride into water containing finely divided manganese peroxide in suspension. The dry peroxide unites at once with sulphurous anhydride to form manganous sulphate :—

$$SO_2 + MnO_2 = SO_2 \cdot O_2Mn,$$

but in the presence of water twice as much of the gas takes part in the reaction, and manganous dithionate is formed :—

$$2SO_2 + MnO_2 = \begin{cases} SO_2 \cdot O \\ SO_2 \cdot O \end{cases} Mn.$$

At the same time a small quantity of the sulphate is always produced, and both salts remain in solution. The filtered liquid is then mixed with a slight excess of baryta water—*i.e.* until it becomes faintly alkaline—which decomposes the manganous sulphate, and precipitates manganous hydrate and barium sulphate. The liquid, which now contains barium dithionate and the excess of barium hydrate, is again filtered, and the slight excess of the latter converted into insoluble barium carbonate by passing a stream of carbonic acid, and at the same time gently warming it. From the clear solution, barium dithionate is deposited in large, colourless crystals on evaporating down, and allowing to cool. If lime water is employed instead of baryta water, calcium dithionate is obtained instead of the barium salt. By decomposing these compounds with the soluble sulphates of other metals, the dithionates of these metals may be easily obtained. All the salts of dithionic acid are soluble in water.

The acid itself may be set free from barium dithionate by exactly precipitating the barium with sulphuric acid, or from the lead salt by precipitating the lead with sulphuretted hydrogen, and then filtering off the clear aqueous solution. The water may be

removed to some extent by evaporation in a vacuum over sulphuric acid; but if the concentration is driven too far, the acid decomposes into sulphuric acid and sulphurous anhydride:—

$$\begin{cases} SO_2\cdot OH \\ SO_2\cdot OH \end{cases} = SO_2 \begin{cases} OH \\ OH \end{cases} + SO_2.$$

The same decomposition takes place when the dilute aqueous solution of the acid is boiled; this may be proved by the odour of sulphurous anhydride and by the precipitate produced on the addition of a drop of barium chloride. But although easily decomposed, dithionic acid is decidedly more stable than thiosulphuric acid.

Dithionic acid is usually thought to be a dibasic acid, although this has not yet been definitely proved. At present only neutral salts of the acid are known, and until we can prepare the acid salts which dithionic acid in common with all polybasic acids ought to yield, the question of its basicity must remain unsettled. Perhaps these compounds are as easily decomposed as the free acid, and break up on evaporation into the acid sulphate and sulphurous anhydride. It is therefore always possible that the molecule of dithionic acid is only half as large as that generally accepted, that it is a monobasic acid and a compound of pentad sulphur (SO_2OH). This possibility is not contradicted by the production and chemical behaviour of the acid, nor is it impossible to imagine that sulphur might exist in some compounds as a pentad element.

POLYTHIONIC ACIDS.

Under this name may be included the three acids of sulphur which contain more than two atoms of sulphur. These are *Trithionic Acid*: $H_2S_3O_6$, *Tetrathionic Acid*: $H_2S_4O_6$, and *Pentathionic Acid*: $H_2S_5O_6$. In these acids it is thought that the two groups of atoms which constitute dithionic acid are united together by one, two, and three atoms of sulphur respectively, as is expressed in the following formulæ:—

$$\text{Trithionic acid} = H_2S_3O_6 = S\begin{cases} SO_2OH \\ SO_2OH \end{cases}$$

$$\text{Tetrathionic acid} = H_2S_4O_6 = S_2\begin{cases} SO_2OH \\ SO_2OH \end{cases}$$

$$\text{Pentathionic acid} = H_2S_5O_6 = S_3\begin{cases}SO_2OH\\SO_2OH\end{cases}$$

formulæ which involve the supposition that the double as well as the triple atom of sulphur can play the part of a diad radical just like a simple atom of the element.

Trithionic Acid : $H_2S_3O_6 = S\begin{cases}SO_2OH\\SO_2OH\end{cases}$

The potassium salt of this acid may be obtained by leading sulphurous anhydride into a solution of potassium thiosulphate, sulphur being at the same time separated :—

$$2SO_2\begin{cases}OK\\SK\end{cases} + 3SO_2 = 2K_2S_3O_6 + S.$$

The acid, which may be set free from the potassium salt by the action of fluosilicic acid, very easily decomposes into sulphur, sulphurous anhydride, and sulphuric acid.

Tetrathionic Acid : $H_2S_4O_6 = S_2\begin{cases}SO_2OH\\SO_2OH\end{cases}$

The sodium salt is obtained by adding iodine to an aqueous solution of sodium thiosulphate :—

$$2SO_2\begin{cases}ONa\\SNa\end{cases} + I_2 = Na_2S_4O_6 + 2NaI.$$

The barium salt may also be prepared in the same way. If this compound is decomposed with sulphuric acid, free tetrathionic acid is produced, which decomposes at a certain stage of concentration into sulphur, sulphurous anhydride, and sulphuric acid. Its salts, which are mostly soluble in water, are decomposed on evaporation into sulphur and the corresponding trithionates.

Pentathionic Acid : $H_2S_5O_6 = S_3\begin{cases}SO_2OH\\SO_2OH\end{cases}$

The free acid is produced together with large quantities of sulphur when sulphuretted hydrogen is led into an aqueous solution of sulphurous acid [1] :—

$$5H_2S + 5SO_2 = H_2S_5O_6 + 5S + 4H_2O.$$

The barium salt may also be prepared by adding sulphur di-

[1] See Appendix.

chloride to water containing finely divided barium thiosulphate in suspension :—

$$2SO_2\left\{\begin{matrix}O\\S\end{matrix}\right.Ba + SCl_2 = BaS_5O_6 + BaCl_2.$$

The free acid, which may be concentrated in a vacuum to a given strength, soon decomposes into sulphur, sulphurous anhydride and sulphuric acid in the same manner as the other two acids.

COMPOUNDS OF SULPHUR WITH CHLORINE.

A chloride of sulphur corresponding to sulphuric anhydride (*i.e.* containing one atom of hexad sulphur united with six atoms of chlorine) has not yet been prepared. That consisting of one atom of sulphur and four of chlorine—sulphur tetrachloride : SCl_4—is a very unstable compound. More stable but still easily decomposed is sulphur dichoride : SCl_2 ; while the most stable compound of all is

Disulphur Dichloride : S_2Cl_2.

This compound is a transparent dark yellow liquid, fuming slightly in the air and possessing a powerful piercing odour. Its specific gravity is 1·7, and it boils at 138°. Disulphur dichloride is easily obtained by heating sulphur in a retort and passing dry chlorine gas over it. The sulphur then melts and the two elements unite with one another, the volatile chloride condensing in the cool receiver. The raw product is contaminated with sulphur dichloride, from which it may be freed by fractional distillation, reserving that portion only which passes over at 138°. Disulphur dichloride is a good solvent for sulphur, of which it dissolves more than half its weight. It is decomposed by water into sulphur, sulphurous anhydride, and hydrochloric acid.

Sulphur Dichloride : SCl_2, is a heavy brown oil with similar properties to the preceding compound. It is obtained by saturating disulphur dichloride with chlorine at the ordinary temperature and then removing the excess of chlorine by passing a stream of dry carbonic anhydride. The compound begins to boil at 64°, due to evolution of free chlorine. It is then decomposed, and partially

even at lower temperatures, into disulphur dichloride and chlorine. Water slowly decomposes it into sulphur, sulphurous anhydride, and hydrochloric acid. Sulphur dichloride forms double compounds with some other chlorides—*e.g.* antimony trichloride, arsenic trichloride, &c.

Sulphur Tetrachloride : SCl_4.

This is a mobile, pale brown liquid produced by saturating either of the other chlorides with chlorine gas at $-22°$. The compound is very unstable and breaks up even below $0°$ into sulphur dichloride and free chlorine.

It is doubtful whether sulphur also unites chemically with bromine and iodine. A *hexiodide* : SI_6, is said to be deposited by allowing a mixed solution of sulphur and iodine in carbon disulphide to gradually evaporate. It is a solid crystalline substance, of dark grey colour, with a metallic lustre, is so easily decomposed that it gradually loses all its iodine when allowed to lie exposed to the air.

SELENIUM.

Chemical Symbol: Se.—*Atomic Weight*: 79.

This element was discovered by Berzelius in 1817, and on account of its similarity to the previously discovered tellurium (from *tellus*, the earth), was named by him selenium (from σελήνη, the moon). Berzelius found the new element in the deposit which had collected on the floor of a sulphuric acid chamber, fed with sulphurous anhydride derived from iron pyrites. Afterwards selenium was also discovered in the flue-dust deposited in the passages through which the acid vapours had to pass to reach the leaden chambers. It was later shown that the element exists, combined with various metals—*e.g.* lead, silver, and mercury—in the mineral kingdom, and just as many samples of iron pyrites contain traces of iron selenide as well as iron sulphide, so too some varieties of native sulphur contain minute quantities of free selenium. Selenium is, however, a rare element, and always difficult to obtain in large quantities.

Selenium which has been melted and allowed to cool is a dark brown amorphous substance with a lustre nearly metallic. It has a *specific gravity* of 4·2, melts at 217°, and boils at about 670°. Its vapour is of a dark yellow colour, and condenses either as bright red flowers of selenium or as a dark metallic-like mass. The specific gravity of its vapour at about 860° is 7·67, but diminishes nearly to that corresponding to the molecule Se_2 (5·58) at about 1400°.

If selenium is reduced from a solution of selenious acid (*e.g.* by sulphurous anhydride) it is deposited as a red amorphous powder. This modification is soluble in carbon disulphide, from which it is again separated on evaporation as dark-red, transparent crystals, isomorphous with monoclinic sulphur. A second crystalline modification is also known which is insoluble in carbon disulphide, has a specific gravity of 4·5, and conducts an electric current feebly; it also possesses the remarkable property of conducting better under the influence of light than in the dark. This form of selenium is prepared by melting the element and keeping the temperature constant at 210°, until it has become crystalline in structure. It then conducts twice as well in diffused daylight, and nearly ten times as well in direct sunlight as in the dark. If the intensity of the light is diminished, the conductivity rapidly decreases.

The extraction of selenium from flue-dust containing it, or from its ores, is a tedious process. The various methods chiefly consist in oxidizing the selenium to selenious acid and then reducing it again by sulphurous anhydride.

Selenium burns when heated in the air with a bright blue flame to form selenious anhydride. It requires, however, a higher temperature for its combustion, and burns more difficultly than sulphur. During combustion it gives off an intense and disgusting odour, which, however, is not peculiar to selenious anhydride, but is probably due to the simultaneous production of small quantities of a lower oxide.

COMPOUNDS OF SELENIUM.

The compounds of selenium are closely related in their chemical properties to those of sulphur. Seleniuretted hydrogen corresponds to sulphuretted hydrogen, selenious anhydride to

sulphurous anhydride, selenic acid to sulphuric acid, and the two chlorides of selenium to disulphur dichloride and sulphur tetrachloride respectively. But, at the same time, many differences may be noted when similar compounds are compared together. Sulphurous anhydride, for example, is a gas, and does not unite with water to form the corresponding acid, while selenious anhydride is a solid crystalline body and easily forms the corresponding selenious acid. Sulphur and sulphurous anhydride are oxidized by nitric acid to sulphuric acid, while nitric acid has no action on selenious acid and only oxidizes selenium to the lower acid. Sulphuric acid can be distilled unchanged, or at least with very slight decomposition; selenic acid breaks up at about 280° into selenious acid and oxygen. Sulphur tetrachloride is a very unstable liquid, decomposing even below 0°; while selenium tetrachloride is a crystalline solid which can be heated without decomposition.

It will thus be seen that considerable differences exist between sulphur and selenium with regard to their affinities for other bodies. It is clear from the facts mentioned above that selenium has a stronger affinity for chlorine and a weaker affinity for oxygen than sulphur, and this is confirmed by the fact that sulphur catches fire and burns when heated in oxygen or air much more easily than selenium.

Still more remarkable is the affinity of selenium for hydrogen, and in this respect again it is at once distinguished from sulphur. Sulphur and hydrogen unite directly with one another only imperfectly, and the resulting sulphuretted hydrogen is very easily decomposed by heat. Selenium, on the other hand, unites with hydrogen at about 500°, forming seleniuretted hydrogen, which is only decomposed into selenium and hydrogen at a high temperature.

Selenium, with the similar elements tellurium and sulphur and the metals of the alkalies, are the only elements which unite directly both with hydrogen and oxygen. Those elements which possess a strong affinity for oxygen—*e.g.* phosphorus, arsenic, silicon, carbon, and most of the metals—cannot unite directly with hydrogen; while the few other elements distinguished by their affinity for hydrogen —*e.g.* chlorine and palladium—cannot combine directly with oxygen.

Seleniuretted Hydrogen: H_2Se.

This compound is a colourless gas with an odour resembling sulphuretted hydrogen, and is exceedingly poisonous. Minute quantities in the air produce painful inflammation of the eyes and nasal passages, loss of the sense of smell, dryness in the throat, and a species of catarrh, often lasting for weeks together. Great care must, therefore, be taken in working with the gas, and in all operations during which it may be set free.

Seleniuretted hydrogen is produced when dry hydrogen gas is led over selenium heated to the temperature at which it commences to volatilize. It may be obtained in larger quantities by acting upon potassium selenide or ferrous selenide with hydrochloric acid. Like sulphuretted hydrogen, the gas is soluble in water, but in larger quantities. This solution reddens litmus paper, colours the skin red from reduced selenium, and becomes oxidized when exposed to the air, selenium being set free. Seleniuretted hydrogen precipitates many metals from solutions of their salts as insoluble selenides, just as sulphuretted hydrogen precipitates insoluble sulphides.

Selenious Anhydride: SeO_2.

This substance is obtained when selenium is heated in a stream of dry oxygen. The selenium burns with a bright blue flame producing the anhydride, which is deposited on the cooler portions of the tube in long, quadrangular, white needles. It sublimes without first melting. Its vapour resembles that of chlorine in colour and possesses a piercing acid odour, the disgusting odour produced when selenium burns in oxygen or air being probably due to some lower oxide. When boiled with water it unites with this substance and forms the corresponding—

Selenious Acid: $SeO\begin{cases}OH\\OH\end{cases}$

This dibasic acid is deposited on cooling the hot saturated aqueous solution in transparent crystalline prisms resembling those of potassium nitrate, and with a strong acid taste. When heated these crystals break up into the anhydride and water. The aqueous solution when made acid with a few drops of hydrochloric acid deposits selenium if warmed with sulphurous anhydride or other reducing agents. Particles of dust of organic origin produce the

same change, so that the lips of glass bottles containing aqueous selenious acid become coloured red from reduced selenium. With *sulphuretted hydrogen selenious acid is decomposed into compounds* of selenium and sulphur, water being also formed.

Selenious acid can also be easily obtained by oxidizing selenium with nitric acid ; after the excess of nitric acid has been expelled it remains behind as a white crystalline mass. Selenic acid is never produced by this reaction.

Selenic Acid: $SeO_2\begin{cases}OH\\OH\end{cases}$

This acid, which corresponds to sulphuric acid in its composition, and which it resembles in many respects, cannot be obtained by oxidizing selenium with nitric acid. It is, however, easily produced by leading chlorine into a strong aqueous solution of selenious acid, or by the oxidation of the latter substance by potassium dichromate. Potassium selenate may also be easily prepared by fusing together either selenium or a compound containing it with potassium nitrate. An aqueous solution of selenic acid may be concentrated until it attains a boiling-point of 265° and specific gravity of 2·6, but further concentration decomposes it into oxygen and selenious acid. (See App.) The strong acid is a colourless, oily liquid, which evolves heat when mixed with water, and is not affected by sulphurous anhydride or sulphuretted hydrogen. It is, however, reduced to selenious acid when boiled with hydrochloric acid, chlorine being evolved.

The selenates closely resemble the sulphates in their properties ; barium selenate, like barium sulphate, is insoluble in water and dilute acids.

Selenium Disulphide : SeS_2.

This compound separates out as a yellow precipitate when sulphuretted hydrogen is led into an aqueous solution of selenious acid. The yellow precipitate gradually coagulates to a red mass, a colour which it retains on drying. If, on the other hand, seleniuretted hydrogen diluted with hydrogen is led into a saturated aqueous solution of sulphurous anhydride, the yellow precipitate consists chiefly of *sulphur diselenide* : SSe_2. Selenium and sulphur may be fused together in any proportion.

Chlorides of Selenium.

Diselenium dichloride: Se_2Cl_2, is prepared in precisely the same manner as disulphur dichloride, which it closely resembles.

Selenium tetrachloride: $SeCl_4$, which is obtained by saturating the preceding compound with chlorine or by distilling selenious anhydride with phosphorus pentachloride, is a solid body, crystallizing in colourless cubes. When heated it sublimes without melting. It dissolves in water and then gradually decomposes into selenious and hydrochloric acids.

TELLURIUM.

Chemical Symbol: Te.—*Atomic Weight*: (?) 127·6.

This extremely rare element was discovered by Müller v. Reichenstein in 1782 in gold ores obtained from Transylvania, but was only exactly studied by Klaproth in 1798, and later by Berzelius in 1832.

It occurs native in the mineral kingdom, but more commonly combined with gold, silver, lead, and bismuth. The mineral *tetradymite* (bismuth telluride) contains about 50 per cent. of tellurium. The ores are found in Hungary and Transylvania, and recently in large quantities at several places in North America.

Tellurium possesses many of the properties of a metal. It has a perfect metallic lustre, is nearly silver white in colour, crystalline in structure (crystallizing in rhombohedra), is brittle, and therefore easily reduced to powder. It conducts heat well, and electricity to some extent. Tellurium melts at about 500°, and can be sublimed at a higher temperature, producing a bright yellow vapour; its specific gravity is 6·4. Carbon disulphide does not dissolve it, but it is soluble in warm concentrated sulphuric acid, forming a magnificent red solution, from which it is again precipitated unchanged as a grey powder when the solution is diluted with water. When strongly heated in the air it burns with a brown flame, bordered with green, forming tellurous anhydride. Hot nitric acid converts it into tellurous acid. (See Appendix.)

Like selenium, tellurium unites directly with hydrogen when heated in a stream of the dry gas, and then produces *telluretted hydrogen*: H_2Te. The same substance is also easily obtained by

acting on zinc telluride with hydrochloric acid. It is a colourless gas with a disgusting odour, similar in its properties and reactions to sulphuretted hydrogen and seleniuretted hydrogen, though not so poisonous as the latter.

The other compounds of tellurium—*tellurous anhydride* and *acid*: TeO_2 and $TeO\begin{cases}OH\\OH\end{cases}$, *telluric acid*: $TeO_2\begin{cases}OH\\OH\end{cases}$, *tellurium di-* and *tetrachloride*: $TeCl_2$, and $TeCl_4$, *tellurium disulphide*: TeS_2 —are closely allied to the corresponding compounds of selenium. The tellurates are, however, very different in their properties from the sulphates and selenates; those of the heavy metals being mostly insoluble in water, while barium tellurate is only difficultly soluble in water and dissolves easily in dilute hydrochloric acid. Double salts of telluric acid corresponding to the alums have not been prepared. On heating telluric acid to a temperature a little below redness, the corresponding anhydride, TeO_3, is obtained. The analogous oxide of selenium is not known.

ELEMENTS OF THE NITROGEN GROUP.

This group consists of the elements nitrogen, phosphorus, arsenic, and antimony. These elements are so different from one another both in their physical properties and their chemical behaviour, as far as the strength of their affinity for other elements is concerned, that it is not at first sight evident why they are placed together in a group. Nitrogen does not catch fire when heated in the air, and it combines so feebly with other substances that it was thought formerly not to unite directly with any other body. Phosphorus, on the other hand, is an easily fusible solid, distinguished by its strong attraction for oxygen, chlorine, and other elements. Arsenic and antimony possess the general physical properties of the metals; they are heavy solids, with a metallic lustre. We shall, however, include these two last-named elements under the non-metals, because their chemical compounds with oxygen, hydrogen, and other elements are closely related to those of nitrogen and phosphorus. And this is also the reason why these four so different elements are included in one group. In most of their compounds the elements of the nitrogen group possess a triad or pentad atomicity.

NITROGEN.

Chemical Symbol: N.—*Atomic Weight*: 14·1.

Nitrogen occurs free in atmospheric air, of which it is the chief constituent; 100 volumes of common air contain about 79 volumes of nitrogen and 21 volumes of oxygen. It also occurs in nature combined with hydrogen as ammonia, and with hydrogen and oxygen as nitric and nitrous acids. From these compounds nitrogen enters into the structure of plants and then of animals. It is a constituent of albumen, casein, blood, and numerous other organic products. Urea, a substance present in large quantities in urine, contains a considerable proportion of nitrogen.

Nitrogen is a colourless gas, without taste or smell, and rather lighter than common air. Its specific gravity is exactly 0·972, which corresponds to a molecular weight of $0·972 \times 28·88 = 28·07$, the molecule containing therefore two atoms (N_2). The gas is only slightly soluble in water. Nitrogen, like hydrogen and oxygen, was formerly called a *permanent* gas; but it has been liquefied by cooling it to $-193°$, and, at a still lower temperature, viz. at $-214°$, nitrogen has even been solidified. (*Comptes rendus*, 100, 350.)

Nitrogen gas may easily be obtained from common air, by abstracting the oxygen which it contains. This may be done by burning a piece of phosphorus in a bell-jar full of air and standing over water. All the oxygen then unites with the phosphorus, producing white vapours of phosphoric anhydride, which afterwards dissolve in the water. As the air cools the water rises in the bell-jar to supply the place of the consumed oxygen, and when the air has become clear it consists almost entirely of nitrogen. A better method, especially when a stream of nitrogen is required, is to pass atmospheric air, which has been previously dried and freed from carbonic acid, over red-hot metallic copper. Finely divided copper, such as copper turnings, is heated to redness in a tube of hard glass while a slow current of the purified air is passed over it. The gas which then escapes at the other end of the tube is pure nitrogen, all the oxygen having combined with the copper to form black copper oxide.

Another method for the preparation of nitrogen consists in

heating a mixture of potassium nitrite and ammonium chloride, which produces ammonium nitrite; this then breaks up into nitrogen and water :—

$$NO \cdot O(NH_4) = N_2 + 2H_2O.$$

Finally, nitrogen is also set free when chlorine gas is led into strong ammonia. In this reaction, hydrochloric acid is produced, which unites with the excess of ammonia, forming ammonium chloride :—

$$8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl.$$

If, however, the chlorine is passed until no more free ammonia is present, the gas then begins to decompose the ammonium chloride, and oily drops of nitrogen chloride, a highly explosive substance, are produced. This process cannot therefore be recommended for the preparation of nitrogen.

Free nitrogen possesses so weak affinities for other elements that it can only be made to combine directly with a very few of them. With oxygen it only unites at the highest temperatures and in the presence of water vapour, producing nitric acid with other lower oxides of nitrogen. Flashes of lightning passing through moist air cause the oxygen and nitrogen to unite and form nitric acid, which can be easily detected in rain water after a thunderstorm.

The direct combination of nitrogen with hydrogen, chlorine, or sulphur, has not yet been effected, and only a very few of the metals combine directly with nitrogen when heated in the gas.

Nitrogen neither supports ordinary combustion nor respiration. A candle immersed in the gas is at once extinguished. At the same time it is not an actual poison, as at once follows from the fact that we respire a mixture of nitrogen and oxygen in common air. An animal when brought into an atmosphere of nitrogen is simply suffocated from lack of oxygen.

COMPOUNDS OF NITROGEN WITH HYDROGEN.

We have already stated that all attempts to unite nitrogen and hydrogen directly with one another have failed. They unite, however, when the two elements are brought into contact with one another in the nascent state.

The simplest compound of nitrogen and hydrogen, viz. *Imidogen* : (NH), is only known in combination with other elements or radicals.

Diamidogen or Hydrazine : N_2H_4 or $H_2N \cdot NH_2$ was prepared by Curtius in 1887 by the decomposition of a somewhat complex carbon compound. The method cannot well be explained without assuming some knowledge, on the part of the reader, of organic chemistry, and is hence

omitted here. Hydrazine is a colourless gas, which fumes in the air, energetically combining with the water present. It has marked basic properties, readily uniting with acids to form salts, such as: $N_2H_4 \cdot HCl$, $N_2H_4 \cdot 2HCl$, &c.

Azoimide or Hydrazoic Acid: N_3H, or $\begin{matrix} N \\ \| \\ N \end{matrix} \!\!> NH$, was first prepared in 1890, also by Curtius. He obtained this acid, by several different methods, from the substance just described; but for a similar reason to that given above, these methods are not detailed here. Azoimide is a light mobile liquid, which boils at 37°, and possesses an intolerable odour. It has a strongly acid and explosive character, the latter being communicated also to its metallic salts. In many other respects, however, azoimide closely resembles the haloid acids.

The compound of nitrogen and hydrogen, which is most readily isolated and is hence best known, is *Ammonia*: NH_3. This is described below.

Finally, the compound of pentad nitrogen with four atoms of hydrogen (NH_4), called *ammonium*, is unknown in the free state, but exists in a large number of compounds very similar to those of the metal potassium.

AMMONIA.

Composition: NH_3.

This compound of nitrogen and hydrogen occurs free in nature and is produced during the putrefaction of nitrogenous organic matter in the absence of strong bases. It is formed, for example, in large quantities in putrefying urine, one constituent of which (urea) then combining with water and breaking up into carbonic anhydride and ammonia.

Ammonia is a colourless gas with a strong, piercing odour, bringing tears to the eyes. It is extremely soluble in water, 1 volume at the ordinary temperature dissolving more than 800 volumes of the gas. This solution, the *liquor ammoniæ* or *spirits of hartshorn* of the shops, possesses the odour of the gas, and reacts powerfully alkaline—*i.e.* turns red litmus paper blue. The gas is considerably lighter than air, its exact specific gravity being 0·589. Its molecular weight is thus $0{\cdot}589 \times 28{\cdot}88 = 17{\cdot}01$, and its molecule is represented by the formula NH_3.

Under a pressure of seven atmospheres at the ordinary temperature, or at −40° under the ordinary pressure, dry ammonia gas becomes converted into a colourless liquid which freezes to a crystalline solid at about −80°.

Ammonia is prepared from the ammonium salts (compounds formed by the union of ammonia with acids), and generally from

ammonium chloride or *sal-ammoniac*. This salt, which can be obtained from ammonia and hydrochloric acid, is decomposed again into these constituents when intimately mixed with strong bases, such as caustic potash, caustic soda or slaked lime, and gently heated. Even when dry ammonium chloride and dry quick-lime are mixed together, ammonia begins to be given off without the mass becoming liquid, whence it follows that the old chemical rule, *only liquids act upon one another*, is not to be taken literally. The reaction goes on according to the equation :—

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3.$$

Calcium chloride and water are thus simultaneously produced, and a portion of the latter passes over with the gas on heating.

In practice, ammonium chloride and quick- or slaked-lime, both finely powdered, are intimately mixed together, and the mixture brought into a glass flask or an iron vessel if large quantities are employed. Heat is then applied and the ammonia dried by passing it through a tube containing pieces of quick-lime. It is then either collected over mercury or by *upward* displacement. The substances generally employed to dry gases—sulphuric acid or calcium chloride—cannot be used for ammonia, as both these bodies absorb large quantities of the gas.

If an aqueous solution of the gas is required, it is of course unnecessary to dry it. It is then sufficient to separate the solid particles which may be carried over with the gas. This is best done by passing the gas through a small quantity of concentrated aqueous ammonia contained in a wash-bottle. Large quantities of heat are evolved when ammonia is absorbed by water, principally due to the latent heat set free when the substance is changed from the gaseous to the liquid form. Care must therefore be taken to cool the vessel containing the water during the absorption of the gas.

The production of ammonia from nitric acid by the action of nascent hydrogen is interesting theoretically. This reduction may be produced in several ways; for example, by the action of dilute nitric acid on zinc. No evolution of hydrogen is noticed, as when zinc is dissolved in sulphuric acid, but the whole of the hydrogen is used to reduce the nitric acid. The ammonia which is formed unites with the excess of acid, producing ammonium nitrate; the zinc is also converted into its nitrate, and water is set free :—

$$2NO_2 \cdot OH \;+\; 4H_2 \;=\; NO_2 \cdot O(NH_4) \;+\; 3H_2O.$$

On adding an excess of caustic soda to the solution, the ammonia is again liberated, and may be easily recognized by its odour.

In order to produce small quantities of liquid ammonia, advantage is taken of the fact that many metallic salts—*e.g.* calcium chloride, silver chloride—absorb ammonia in large quantities and liberate the gas again on warming. Dry silver chloride saturated with dry ammonia is placed in the closed end, *a*, of a thick walled bent glass tube, and the open end, *c*, is then melted together (fig. 47). If now the limb *c* is placed in a freezing mixture, and *a* gently warmed, gaseous ammonia is liberated in large quantities from the silver chloride and is condensed to a colourless liquid in the cold part of the tube. When the tube cools again, the silver chloride reabsorbs the whole of the ammonia, and the experiment may therefore be repeated several times with the same tube.

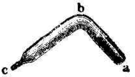


Fig. 47.

Although ammonia contains a large quantity of hydrogen, it does not catch fire in the air, but in oxygen gas it burns with a pale yellowish flame, forming water and free nitrogen. At a high temperature it is decomposed into its constituents, hydrogen and nitrogen. If the gas is led through a porcelain tube filled with broken fragments of the same and heated to bright redness, the volume of the gas becomes doubled :—

$$\underset{4\text{ vols.}}{2NH_3} \;=\; \underset{2\text{ vols.}}{N_2} \;+\; \underset{6\text{ vols.}}{3H_2}.$$

The same decomposition occurs when electric sparks are allowed to pass through the gas for a long time.

Ammonia combines readily with acids and produces real salts, which closely resemble the corresponding compounds of potassium. These are the ammonium salts and contain the monad radical ammonium (NH_4), which plays the part of a metal. When, for example, ammonia unites with hydrochloric acid :—

$$NH_3 \;+\; HCl \;=\; (NH_4)Cl,$$

we consider that the hydrogen of the acid first unites with the nitrogen, and that the ammonium so produced then forms with the chlorine the haloid salt. In a similar manner ammonia also unites with the oxy-acids, but in these compounds the ammonium is united to the acid radical by an atom of oxygen, thus :—

$$\underset{\text{Nitric acid}}{NO_2 \cdot OH} + NH_3 = \underset{\text{Ammonium nitrate}}{NO_2 \cdot O(NH_4)}$$

$$\underset{\text{Sulphuric acid}}{SO_2 \begin{cases} OH \\ OH \end{cases}} + 2NH_3 = \underset{\text{Ammonium sulphate}}{SO_2 \begin{cases} O(NH_4) \\ O(NH_4) \end{cases}}$$

$$\underset{\text{Sulphuric acid}}{SO_2 \begin{cases} OH \\ OH \end{cases}} + NH_3 = \underset{\text{Acid ammonium sulphate}}{SO_2 \begin{cases} OH \\ O(NH_4). \end{cases}}$$

Ammonia also combines with the acid anhydrides, in which the hydrogen necessary to convert it into ammonium is absent. Two molecules of ammonia are then decomposed into one molecule of ammonium and one of amidogen :—

$$2NH_3 = NH_4 + NH_2,$$

which unite with the anhydride (*e.g.* CO_2 or SO_2) to form ammonium compounds of monobasic amido-acids :—

$$CO_2 + 2NH_3 = \underset{\text{Ammonium carbamate}}{CO \begin{cases} NH_2 \\ ONH_4 \end{cases}}$$

In all cases when gaseous ammonia comes into contact with a *gaseous acid, heavy white fumes are produced of the ammonium* salt. This affords a ready test for small quantities of free ammonia. If a glass rod dipped in concentrated hydrochloric acid is brought near the surface of a liquid containing free ammonia, white fumes of ammonium chloride are at once produced. If the ammonia is combined with an acid, as an ammonium salt, it must first be set free by warming with caustic soda or potash.

Chlorine at once decomposes ammonia, forming hydrochloric acid, which then combines with the excess of ammonia to form ammonium chloride (p. 182).

HYDROXYLAMINE—(OXYAMMONIA).

Composition : $NH_2 \cdot OH$.

In hydrogen peroxide we have already become acquainted with a monad radical—hydroxyl—having the composition HO (p. 90). We meet with this hydroxyl in a large number of compounds, particularly in organic chemistry, in which it displaces other monad

elements or radicals, especially hydrogen. And we may look upon hydrogen peroxide as water in which one atom of hydrogen is displaced by hydroxyl, thus : $O\left\{\begin{matrix}OH\\H\end{matrix}\right.$

In precisely the same manner, hydroxyl can also displace one of the atoms of hydrogen in ammonia, and so form the substance hydroxylamine, or oxyammonia.

Oxyammonia has not yet been prepared in the pure state;[1] it is only known in aqueous solution and in combination with acids. It possesses similar properties to those of ammonia, unites with acids producing the oxyammonium salts, but is less volatile. Its aqueous solution is colourless and reacts strongly alkaline.

Oxyammonia is easily produced by the reduction of nitric oxide or higher oxides of nitrogen with nascent hydrogen. For this purpose nitric oxide is led into a mixture of granulated tin and hydrochloric acid, to which a few drops of platinic chloride have been added to accelerate the evolution of hydrogen. The acid liquid then contains stannous chloride together with oxyammonium chloride ; it is freed from tin by passing a stream of sulphuretted hydrogen through it, and the filtered liquid evaporated to dryness. The dry mass is then extracted with absolute alcohol, which dissolves the whole of the oxyammonium chloride, together with a small quantity of ammonium chloride (easily removed by a few drops of platinic chloride). The clear alcoholic liquid on evaporation then yields colourless crystals of oxyammonium chloride : $NH_3(OH)Cl$.

From the chloride the sulphate : $SO_2(ONH_3OH)_2$, is easily prepared by adding to it the requisite quantity of dilute sulphuric acid and evaporating off the hydrochloric acid thus set free. Free oxyammonia may then be obtained by adding baryta water to the aqueous solution of the sulphate as long as a turbidity of barium sulphate is produced. The filtered alkaline solution then contains free oxyammonia.

If this solution is distilled a portion of the oxyammonia passes over with the water vapour, but the greater part is decomposed into ammonia, nitrogen, and water :—

$$3NH_2{\cdot}OH = NH_3 + N_2 + 3H_2O.$$

The aqueous solution of oxyammonia powerfully reduces many compounds. Silver and mercury are precipitated from the solutions of their salts in the metallic state, and with copper sulphate it gives an orange-coloured precipitate of cuprous oxide.

[1] See note in Appendix on p. 387.

Oxyammonia is also produced when some metals, especially zinc, are acted upon by sulphuric acid in the presence of nitric acid. The nascent hydrogen which is then set free reduces a part of the nitric acid to ammonia and oxyammonia. If zinc is used the solution contains the nitrates of zinc, ammonium, and oxyammonium, and on the addition of excess of caustic potash and a few drops of copper sulphate gives an orange-coloured precipitate of cuprous oxide.

The oxyammonium salts, like those of ammonium, are all soluble in water, and can easily be obtained in the crystalline form.

AMIDOGEN : NH_2; IMIDOGEN : NH.

These are two unsaturated compounds of triad nitrogen, the first being a monad, and the second a diad radical. Both occur principally in organic compounds, but amidogen is also known in some inorganic compounds; for example, in the amido-acids. Diamidogen : $H_2N{\cdot}NH_2$, has also been isolated, and is described on p. 183.

AMMONIUM : NH_4.

This unsaturated compound of pentad nitrogen has not yet been prepared in the free state. It is the radical of the ammonium salts, but all attempts to separate it, or rather its molecule : $(NH_4)_2$, have resulted in a mixture of ammonia and hydrogen.

It is very probable that, should this body ever be obtained in the free state, it would be found to possess the properties of a metal. Not only have its compounds the greatest similarity with those of potassium and sodium, but it can also unite in the nascent state with mercury to form an amalgam—a property peculiar to the metals. Ammonium amalgam, with metallic lustre and other remarkable properties, is easily obtained by adding sodium amalgam to a warm, moderately concentrated solution of ammonium chloride. The sodium amalgam immediately swells up to a large extent, at the same time retaining its metallic lustre, and the mass becomes so light that it floats on the surface of the liquid, notwithstanding the mercury which it contains.

The reaction simply consists in the substitution of sodium for ammonium in the ammonium chloride, forming sodium chloride, and setting the ammonium free. The amalgam is very unstable, breaking up immediately into ammonia, hydrogen, and mercury,

the first-named substance being at once recognized by its characteristic odour.

The low specific gravity of the ammonium amalgam makes it probable that if the ammonium itself were separated, it would be a light liquid or a gas.

OXIDES AND OXY-ACIDS OF NITROGEN.

Nitrogen and oxygen unite in five different proportions, and produce as many different compounds. These compounds have the following names and symbols. Two of them (nitrous anhydride and nitric anhydride), unite with water and form the corresponding acids :—

Nitrous oxide . . .	N_2O	Hyponitrous acid (?)	$N{\cdot}OH$
Nitric oxide . . .	NO		
Nitrous anhydride . .	N_2O_3	Nitrous acid	$NO{\cdot}OH$
Nitric peroxide .	N_2O_4		
Nitric anhydride	N_2O_5	Nitric acid	$NO_2{\cdot}OH$

NITRIC ACID.

Composition : $HNO_3 = NO_2{\cdot}OH$.

Nitric acid occurs free in the atmosphere, especially after thunderstorms, and is produced directly from its elements by the high temperature of the flashes of lightning. Its salts are also produced in nature, when nitrogenous organic substances putrefy in contact with strong bases (*e.g.* potash, soda, lime).

Nitric acid is a colourless, strongly acid liquid, fuming in the air. It has a specific gravity of 1·530, boils at 86°, and becomes solid at $-50°$; it mixes with water, with evolution of heat, in all proportions. The acid is not very stable, and is even partially decomposed by light into oxygen and lower oxides of nitrogen, which impart a yellow tint to it. It destroys the skin and other animal substances and colours them yellow, and, in consequence of the ease with which it breaks up into oxygen and the lower oxides of nitrogen, is an excellent oxidizing agent, especially for the metals.

Nitric acid, as we have previously remarked (p. 182), is produced directly from its elements when electric sparks pass through moist air, or when a mixture of hydrogen and excess of oxygen, with

traces of nitrogen, is exploded, or when hydrogen burns in oxygen mixed with a small quantity of nitrogen.

The acid is always obtained from one of its salts—potassium or sodium nitrate—by decomposing it with sulphuric acid. On the small scale pure nitre (potassium nitrate) is powdered and introduced into a retort furnished with a cooled receiver. It is then *mixed with concentrated sulphuric acid and gently heated*, when the whole melts to a homogeneous liquid. As the temperature rises, the nearly colourless acid distils over, and is condensed in the receiver. It is best to employ one molecule of nitre (101), to one molecule of sulphuric acid (98)—*i.e.* about equal parts by weight. The reaction is then represented by the following equation:—

$$\underset{\text{Potassium nitrate}}{NO_2 \cdot OK} + SO_2\begin{cases}OH\\OH\end{cases} = NO_2 \cdot OH + \underset{\text{Acid potassium sulphate}}{SO_2\begin{cases}OH\\OK\end{cases}}$$

If we employ twice as much nitre so as to produce the normal sulphate, the first stage of the reaction goes on as before, but the acid potassium sulphate which remains behind is then mixed with one-half of the nitre employed. At a higher temperature these two substances act upon one another, forming another molecule of nitric acid and normal potassium sulphate:—

$$\underset{\text{Acid potassium sulphate}}{SO_2\begin{cases}OH\\OK\end{cases}} + NO_2 \cdot OK = \underset{\text{Normal potassium sulphate}}{SO_2\begin{cases}OK\\OK\end{cases}} + NO_2 \cdot OH.$$

The temperature at which this takes place is so high that the nitric acid undergoes a partial decomposition into oxygen, nitric peroxide, and water. The oxygen passes off, but the nitric peroxide, a dark red gas, is mostly absorbed by the nitric acid. The acid then becomes of a reddish colour, and gives off brown vapours. This acid is known as *fuming nitric acid*. In order to obtain a pure acid, it is best to take a small excess of sulphuric acid, and then redistil the acid with an equal volume of concentrated sulphuric acid. The strong attraction of sulphuric acid for water then frees the nitric acid of this impurity.

Commercial nitric acid is now often prepared from Chili saltpetre ($NaNO_3$), this salt being much cheaper than ordinary nitre, and yielding weight for weight a greater quantity of nitric acid. It is usually coloured yellow, and is often contaminated with chlorine,

iodine, sodium sulphate, and iron. These impurities may be readily separated by repeated distillation, neglecting the first and last portions which come over. It always contains water, the quantity of which may be determined by means of an hydrometer. The greater the quantity of water the lower the specific gravity. The specific gravity of this commerical acid is often as low as 1·33, and then contains only about 50 per cent. of the pure acid.

The specific gravity of the pure acid is, as we have stated above, 1·530. An acid which has a specific gravity of 1·424, and which boils at about 120°, contains nearly 70 per cent. of pure acid. The dilute acid, of specific gravity 1·2, which is employed in the laboratory for general purposes, contains only 32 per cent. of the pure acid.

If concentrated nitric acid containing more than 70 per cent. of the pure acid is boiled under the ordinary atmospheric pressure, the portion which distils over contains less water than that in the retort until the boiling-point rises to about 120°, when the composition of the distillate and of the residue in the retort remains nearly constant. This acid of constant boiling-point has a specific gravity of 1·42, and contains about 70 per cent. of pure acid. Further, if dilute nitric acid containing less acid than 70 per cent. is distilled, the portion which passes over is at first more dilute than that in the retort, and rises in strength until it contains about 70 per cent. of pure acid, when the composition again remains nearly constant. It must not, however, be supposed that this particular mixture is a chemical compound of water and nitric acid. That it is not so is proved by the fact that if the pressure is changed the composition of the distillate changes also.

Nitric acid is a solvent for many substances which are insoluble in water—particularly for the metals. Among the few metals which withstand its action are gold and platinum. Silver is at once attacked by it and converted into the soluble nitrate, a portion of the nitric acid being reduced to nitric oxide, producing red fumes of nitric peroxide in the air. The reaction goes on according to the following equation, which also represents the oxidation of many other metals by nitric acid :—

$$4NO_2{\cdot}OH + 3Ag = 3NO_2{\cdot}OAg + 2H_2O + NO.$$

In consequence of this property of nitric acid to dissolve silver but not gold, nitric acid has been long employed to separate the two metals from one another.

Nitric acid is a monobasic acid, as it only contains one atom of displaceable hydrogen; it, therefore, only produces normal salts. The *nitrates* are all soluble in water, and we cannot therefore recognize them, as we can the sulphates, by the production of one which is insoluble in water. All nitrates are decomposed by strong sulphuric acid yielding nitric acid; and if a solution of a nitrate is mixed with sulphuric acid and copper turnings and then warmed, the nitric acid which is set free acts on the copper and produces nitric oxide, which at once gives rise to brown fumes of nitric peroxide and nitrous anhydride on coming into contact with the oxygen of the air. Another delicate test for a nitrate is mentioned under nitric oxide.

Nitric Anhydride N_2O_5.

This substance, as its name implies, is nitric acid minus the elements of water, and may be considered as two molecules of nitric peroxide united by an atom of oxygen, thus $\left.\begin{matrix} NO_2 \\ NO_2 \end{matrix}\right\} O$.

It is obtained in colourless lustrous crystals belonging to the rhombic system when finely-powdered dry silver nitrate is dropped into a flask containing dry chlorine. The two substances then react upon one another, producing nitric anhydride, silver chloride, and oxygen. On opening the flask afterwards the oxygen and excess of chlorine are got rid of by blowing in dry air, and the anhydride, which melts at 30°, is then easily separated from the silver chloride by gentle heating. If heated slightly above its boiling point (45°), it decomposes with explosion into nitric peroxide and oxygen, and the decomposition also goes on slowly in sealed tubes. It readily dissolves in water, evolving heat, and producing nitric acid :—

$$\left.\begin{matrix} NO_2 \\ NO_2 \end{matrix}\right\} O \quad + \quad H_2O \quad = \quad 2NO_2{\cdot}OH.$$

NITRIC OXIDE.

Composition: NO.

This oxide of nitrogen is a colourless gas, slightly soluble in water, and with a specific gravity of 1·039. This density corresponds to a molecular weight of $1{\cdot}039 \times 28{\cdot}88 = 30$, whence its composition.

Nitric oxide possesses none of the acid properties of nitric acid. It is distinguished from all other gaseous bodies by its remarkable property of combining directly with oxygen at the ordinary temperature to form a dark red gas. From this it follows that nitric oxide may at once be recognized by the red colour produced when it comes into contact with common air. This red gas is either nitrous anhydride or nitric peroxide, according to the quantity of oxygen present.

Nitric oxide is obtained from nitric acid by abstracting a portion of its oxygen by copper or some other similar metal. Small pieces of copper are placed in a flask and then dilute nitric acid, of specific gravity 1·23, poured over them. The gas soon begins to be given off, and the mixture evolves large quantities of heat, and if the flask is not cooled from time to time by dipping it into cold water, the reaction may become so violent that the liquid froths over. The nitric oxide which is first produced unites at once with the oxygen of the air in the flask and forms red fumes of nitrous anhydride, but as this compound is absorbed by water, the gas when collected in a jar over water soon becomes colourless. After a time, when the whole of the air has been expelled from the flask, pure colourless nitric oxide is given off. The reaction may be considered as taking place in two stages. In the first the copper is oxidized to copper oxide, and the nitric acid reduced to nitric oxide and water; while, in the second, the copper oxide unites with the excess of nitric acid to form copper nitrate. The entire reaction is expressed in the following equation:—

$$3Cu + 8NO_2 \cdot OH = 3\left.\begin{matrix} NO_2 . O \\ NO_2 . O \end{matrix}\right\} Cu + 2NO + 4H_2O.$$

If the mixture of copper and nitric acid becomes too hot the nitric oxide may easily become contaminated with nitrous oxide. Instead of copper we may also use mercury or silver for the preparation of nitric oxide; but all metals cannot be employed, some give off nitrous anhydride or nitric peroxide.

In nitric oxide the constituents are firmly united together, much more firmly than in nitrous oxide, which contains half as much oxygen. A glowing chip of wood, faintly glowing charcoal, or burning sulphur is at once extinguished in the gas, but strongly glowing charcoal continues to burn brilliantly. Phosphorus can be melted in the gas without catching fire, but ignited phosphorus goes on burning. In all cases when substances burn in

nitric oxide the temperature of combustion must be high enough to decompose the gas into its constituents. Among the more easily combustible substances, the volatile liquid carbon disulphide is distinguished by the readiness with which it burns when mixed with nitric oxide. A small quantity of the disulphide is poured into a jar of the gas closed with a glass plate, the jar slightly agitated so as to volatilize the disulphide, and the mixture then ignited. The carbon disulphide then burns with so brilliant a flame that it can scarcely be borne by the naked eye.

Strong as well as dilute nitric acid dissolves considerable quantities of nitric oxide and becomes coloured brown, yellow, green, or blue according to the concentration of the acid. A solution in the concentrated acid (specific gravity 1·35) is brown, in an acid of specific gravity 1·25 is blue. On heating the acid the nitric oxide is again given off.

Ferrous sulphate dissolved in water also absorbs nitric oxide, yielding a brown solution; this property is used to detect the presence of nitric acid or of a nitrate. To the given solution is added about its own volume of a solution of ferrous sulphate, both being cold; the mixture is then poured into a test-tube, and an equal volume of concentrated sulphuric acid is carefully poured down the side of the inclined tube. The acid thus collects at the bottom of the tube, and where the two liquids come into contact a brown layer appears, if a nitrate is present. The sulphuric acid sets the nitric acid free; this is reduced by the ferrous sulphate to nitric oxide, and the excess of this reagent dissolves the nitric oxide, so producing the brown layer.

NITROUS ANHYDRIDE AND NITRIC PEROXIDE.

These two oxides of nitrogen, which are intermediate between nitric acid and nitric oxide in composition, are so similar in the gaseous state, that one can scarcely be distinguished from the other, especially as they are generally produced together. Both are brown gases, with a strong unpleasant odour, and both are produced by the union of nitric oxide with oxygen—when the nitric oxide is in excess, nitrous anhydride is formed, and with excess of oxygen nitric peroxide. Both gases can be easily condensed to the liquid state by lowering the temperature; liquid nitrous anhydride is blue, while liquid nitric peroxide is pale brown.

A mixture of nitrous anhydride and nitric peroxide is easily obtained by heating arsenious anhydride, white arsenic (in lumps) with nitric acid of specific gravity 1·33. When the reaction has once been started it goes on without further heating until finished, oxygen being abstracted from the nitric acid while the arsenious anhydride is oxidized to arsenic acid. The red gases are led through a tube surrounded by a freezing mixture and are there condensed to a deep blue liquid. This liquid begins to boil at + 2°, and the boiling point gradually rises to 22°. It is a mixture of the volatile nitrous anhydride, and the less volatile nitric peroxide. From this mixture the two substances may be easily obtained in the pure state.

Nitrous Anhydride : N_2O_3.

This substance is obtained from the blue liquid mentioned above by passing its vapour mixed with nitric oxide through a red-hot glass tube. The nitric peroxide which it contains then unites directly with the nitric oxide to form nitrous anhydride : $NO_2 + NO = N_2O_3$, which can be condensed in a freezing mixture to an indigo-coloured liquid. This liquid does not solidify at − 30° and begins to boil below 0°, while at higher temperatures it easily decomposes into nitric peroxide and nitric oxide. Nitrous anhydride dissolves in a small quantity of ice-cold water and forms

Nitrous acid : $NO \cdot OH$, according to the equation : $N_2O_3 + H_2O = 2NO \cdot OH$. It easily decomposes when slightly warmed into nitric acid, nitric oxide, and water :—

$$3NO \cdot OH = NO_2OH + 2NO + H_2O.$$

More stable than the acid itself are its compounds—the *nitrites.* Potassium nitrite ($NO \cdot OK$), which contains one atom of oxygen less than potassium nitrate ($NO_2 \cdot OK$), is easily produced by fusing the latter substance until the oxygen which is given off begins to be mixed with nitrogen. The potassium nitrite can then be extracted from the powdered mass by means of alcohol, in which it is soluble.

If potassium nitrite, or any other salt of nitrous acid, is treated with dilute sulphuric acid, it is at once decomposed ; the nitrous acid which is thus set free imparts a transient blue colour to the liquid, but soon breaks up with evolution of red vapours. An aqueous solution of potassium nitrite when mixed with silver nitrate produces a white precipitate of silver nitrite, thus :—

$$NO \cdot OK + NO_2 \cdot OAg = NO \cdot OAg + NO_2 \cdot OK.$$

Ammonium nitrite ($NO \cdot ONH_4$), which, it will be remembered, breaks up into water and nitrogen when heated (p. 182), is also produced in *minute* quantities when water rapidly evaporates, a portion of the water then uniting with the nitrogen of the atmosphere :—

$$2H_2O + N_2 = NO \cdot ONH_4.$$

The same compound is also produced when ammonia is oxidized by a mixture of ozone and oxygen :—

$$2NH_3 + O_3 = NO \cdot ONH_4 + H_2O,$$

and the salt is then further oxidized to ammonium nitrate.

Nitric Peroxide : $(NO_2)_2 = N_2O_4$.

This compound of nitrogen and oxygen possesses all the properties of a compound radical, and resembles chlorine in many respects. A more suitable name for it than nitric peroxide would be *nitryl*, corresponding to hydroxyl, sulphuryl, &c.

Nitric peroxide is best obtained from the crude blue liquid referred to on the preceding page. When this liquid is kept in a freezing mixture and a current of oxygen led through it the nitrous anhydride which it contains becomes oxidized, and pure nitric peroxide is obtained. Nitric peroxide may also be prepared by leading a mixture of nitric oxide and excess of oxygen into a cooled tube, or, finally, by carefully heating dried lead nitrate in a retort, when the salt suffers the following decomposition :—

$$\left.\begin{matrix} NO_2 \cdot O \\ NO_2 \cdot O \end{matrix}\right\} Pb = (NO_2)_2 + O + PbO.$$

Nitric peroxide is a pale brown liquid, of specific gravity 1·45 ; it boils at 22° and then forms a brown gas, which becomes of a darker colour when heated. It freezes at $-20°$ to a colourless crystalline mass, which again melts at about $-12°$. The vapour density of nitric peroxide at low temperatures has been found to be 2·65, at high temperatures 1·58. The former number approaches the density required for the formula N_2O_4, which would be $\frac{(2 \times 14) + (4 \times 16)}{28 \cdot 88} = \frac{92}{28 \cdot 88} = 3 \cdot 183$, while that of the latter is about one-half of this, or corresponds to the molecule NO_2.

From this we conclude that at low temperatures the molecule of nitric peroxide is composed of twice NO_2 or $NO_2 \cdot NO_2$, which, when

heated to 100°—150°, breaks up into separate molecules of the composition NO_2. The same change probably takes place when many elements—*e.g.* oxygen or chlorine—are raised to a very high temperature. The atoms, which at ordinary temperatures are united to form molecules, then divide into separate atoms and so acquire a far stronger power of affinity than in the ordinary molecular state. In the same way nitric peroxide unites much more readily with other bodies at 100° than at the ordinary temperature; for example, it can then combine directly with chlorine, bromine, cyanogen, &c.

Concentrated, colourless nitric acid dissolves large quantities of nitric peroxide, producing the red or fuming nitric acid. This acid is a much more powerful oxidizing agent than ordinary nitric acid, because the nitric peroxide which it contains parts with a portion of its oxygen far more readily than nitric acid itself.

In contact with cold water nitric peroxide is decomposed into nitric and nitrous acids :—

$$(NO_2)_2 \quad + \quad H_2O \quad = \quad NO_2\cdot OH \quad + \quad NO\cdot OH\ ;$$

the nitrous acid gradually decomposing into nitric acid, nitric oxide, and water (p. 195).

Chlorine, which at low temperatures is without action on nitric peroxide, combines with it when a mixture of the two gases is led through a heated tube, producing *nitryl chloride* : NO_2Cl, a yellow liquid boiling at +5°, which is decomposed by water into nitric and hydrochloric acids. (See Appendix.)

The same compound is also produced by leading a stream of chlorine over gently heated silver nitrate :—

$$NO_2\cdot OAg \quad + \quad Cl_2 \quad = \quad NO_2Cl \quad + \quad AgCl \quad + \quad O.$$

If liquid sulphurous acid and nitric peroxide are heated together in sealed bes, or if nitric oxide is allowed to act upon sulphuric anhydride, a crystalline compound is produced, of the composition : $S_2O_5\cdot 2NO_2$, or $O\begin{cases}SO_2\cdot NO_2\\SO_2\cdot NO_2\end{cases}$, and which may be considered either as the dinitryl of disulphuric acid, or as the anhydride of the next following substance, nitrosulphonic acid. This compound melts at 217°, and is decomposed by water into sulphuric acid, nitric oxide, and nitric peroxide.

Concentrated sulphuric acid absorbs nitric peroxide and produces white crystalline *nitrosulphonic acid*: $SO_2\begin{cases}NO_2\\OH\end{cases}$ p. 166), in

which one atom of hydroxyl is displaced by one of nitric peroxide, nitric acid being probably formed at the same time. This compound is also decomposed by water into sulphuric acid, nitric oxide, and nitric peroxide.

Aqua Regia.—This liquid, which owes its name to its property of dissolving gold, the king of metals, as well as platinum, is a mixture of three parts of hydrochloric acid and one part of nitric acid. The two acids act upon one another at the ordinary temperature, the mixture becoming yellow and giving off minute bubbles of gas smelling like chlorine. This gas, which is evolved in quantity on gently warming, is a mixture of chlorine and *nitrosyl chloride*: NOCl. In the nascent state the latter substance gives up its chlorine to the gold or platinum, producing soluble chlorides of these metals. The reaction by which it is produced is shown by the following equation :—

$$NO_2 \cdot OH + 3HCl = NOCl + 2H_2O + Cl_2.$$

NITROUS OXIDE.

Composition: N_2O.

This substance is a colourless, odourless gas, with a somewhat sweet taste, and a density of 1·52, which corresponds to a molecular weight of 43·9. Under strong pressure (thirty atmospheres at 0°) it is condensed to a colourless liquid, which is lighter than water, and with which water does not mix. The liquid boils at about −92°, and when allowed to evaporate, rapidly solidifies to a white crystalline solid. Nitrous oxide is only slightly soluble in water, and can, therefore, be collected over this liquid.

The gas is easily prepared by heating crystallized ammonium nitrate in a retort. The salt then melts and completely decomposes, with much frothing and apparent boiling, into nitrous oxide and water. Thus :—

$$NO_2 \cdot ONH_4 = N_2O + 2H_2O.$$

It is not advisable to decompose the whole of the salt employed, as overheating may cause the nitrous oxide to decompose into its constituents with an explosion. This method quickly yields large quantities of pure nitrous oxide, if care is taken that the ammonium

nitrate contains no ammonium chloride, otherwise the gas becomes contaminated with chlorine compounds. Nitrous oxide is also produced when zinc or one of a few other metals is dissolved in very dilute nitric acid. The gas obtained in this way is, however, never pure, but always contains more or less nitric oxide.

The most remarkable property of nitrous oxide is the readiness with which it allows combustible bodies to burn in it. Combustion takes place in the gas almost as energetically as in pure oxygen, much more so than in nitric oxide, although this gas contains twice as much oxygen. From this we conclude that the nitrogen and oxygen are much more loosely combined in nitrous oxide than in nitric oxide. In fact, nitrous oxide is decomposed into its constituents even when passed through a red-hot tube. A glowing chip of wood catches fire in nitrous oxide almost as easily as in oxygen. Phosphorus and charcoal burn brilliantly, and sulphur, if strongly ignited, continues to burn with a bright flame. Feebly burning sulphur is extinguished in the gas, because the temperature is not high enough to decompose it into its constituents. That nitrous oxide, although a chemical compound of nitrogen and oxygen, supports combustion much better than the mechanical mixture of the same two substances which make up common air is partly because the compound contains thirty-three per cent. by volume of oxygen, while common air has scarcely more than twenty per cent. by volume, and is partly due to the fact that when nitrous oxide is decomposed a considerable quantity of heat is set free.

Nitrous oxide is chemically an indifferent body, and does not enter into combination with any substance. Its peculiar property of producing intoxication when inhaled is of physiological interest. When breathed in small quantities it produces a pleasurable nervous excitation, whence its common name of *laughing-gas.* But if mixed with atmospheric air and inhaled for some time it produces, like chloroform, temporary insensibility, and without the unpleasant after-effects of the latter substance. It is largely used for minor surgical operations, particularly in dentistry, to produce insensibility to pain and to allow the surgeon to operate more easily.[1] (See also Appendix.)

[1] The composition of nitrous oxide and of nitric oxide may be easily determined by burning a small piece of potassium in a given volume of the gas, standing over mercury. The gas is thus decomposed, its oxygen uniting with the potassium, and the nitrogen being set free. Nitrous oxide is then found to contain its own volume of nitrogen and nitric oxide one-half its volume, whence the formulæ N_2O and NO may be easily deduced.—ED.

ATMOSPHERIC AIR.

Although the atmosphere is not a chemical compound, it is scarcely of less interest and importance to the chemist than water. The importance of the atmosphere for chemistry and other allied sciences is at once evident when we remember that the air has always played a large part in building up and in disintegrating the solid crust of the earth, that all processes of combustion or oxidation on the earth's surface are supported by it, that its constituents nourish both plants and animals, and that the state of health of individuals as well as of entire communities depends upon the purity of the air as well as of the water supplied to them.

We have already learnt that atmospheric air deprived of its other admixtures consists of about 21 volumes of oxygen mixed with about 79 volumes of nitrogen. Besides these two gases atmospheric air always contains very varying quantities of water vapour, small quantities of carbonic acid (about 3 volumes per 10,000), and traces of ammonia (a few parts per million). The composition of atmospheric air by volume, taking the mean quantity of water-vapour, is then :—

Nitrogen	= 77·19	volumes
Oxygen	= 20·66	„
Water (mean)	= 1·40	„
Carbonic acid	= 0·03	„
Ammonia	= traces.	
	100·00	volumes.

These numbers lead to several interesting questions, the first of which is whether the nitrogen and oxygen contained in atmospheric air are chemically united or only mechanically mixed. If we abstract the water vapour and carbonic acid from the air, the proportion of nitrogen and oxygen then becomes :—

Nitrogen	= 79·04	volumes
Oxygen	= 20·96	„
	100·00	volumes,

and it has been found that ever since the composition of the air has been accurately known, this proportion has not appreciably varied, and that whether the air is taken from over the sea, from the surface of the earth inland, or from high mountain tops, even

as high as 14,000 feet above the sea-level, the proportion of nitrogen and oxygen is always almost exactly the same. This speaks strongly for the supposition that the two gases are chemically united in atmospheric air.

But in spite of this we know for certain that the gases are only mixed together—that they do not form a chemical compound in the atmosphere. This conclusion is supported by the following facts :—

i. If we mix together 21 volumes of oxygen with 79 volumes of nitrogen, we obtain a gas which possesses all the properties of common air deprived of its water and carbonic acid. But we notice no elevation of temperature, which would certainly take place had the gases combined together chemically.

ii. If cold boiled water is shaken up with atmospheric air, the water takes up more oxygen than nitrogen, and the air which remains behind is then poorer in oxygen than common air. Or, if common air is passed through a porous tube more of the lighter nitrogen diffuses through in a given time than the heavier oxygen. Neither of these partial separations of the nitrogen and oxygen in common air could take place if the two substances were chemically united.

iii. Finally, every chemical compound contains its constituents not only in a fixed proportion, but also in weights which are some simple multiple of the atomic weight of its constituents. Atmospheric air contains its nitrogen and oxygen in nearly constant proportion by volume and weight, but not in simple atomic proportions. The composition of air by weight is :—

Nitrogen	77 parts
Oxygen	23 „
	100 parts,

and if we divide these numbers by the respective atomic weights of the elements, we obtain the ratio :—

$$\frac{77}{14} : \frac{23}{16} = 5{\cdot}55 : 1{\cdot}44 = 3{\cdot}85 : 1,$$

a ratio which, although it approaches 4 : 1, is far from being a simple one, as it would be in a chemical compound. The difference in the composition of the air, and of a compound containing four atoms of nitrogen and one of oxygen, becomes more apparent if we calculate the percentage composition of this unknown body [N_4O]. We find it to be :—

$4N$	= 56	. . . . . .	= 77·8 per cent.
O	= 16	. . . . . .	= 22·2 „
	72		100·0

According to which the air contains 0·8 per cent. nitrogen less, and 0·8 per cent. oxygen more than this unknown compound, a difference which is much too great to be ascribed to experimental errors, especially as the methods employed for the analysis of such simple gaseous mixtures leave nothing to be desired in exactness, and indeed exceed in this respect almost all other analytical methods.

A further and much disputed point is whether the atmospheric air has always possessed the same composition which it does at present, and whether its composition will not change in the course of ages. The occurrence of nitrogen in the mineral kingdom as nitre, with that which is contained in the substance of plants and animals, is so extremely minute compared with the immense quantities of nitrogen in the air that little change has probably taken place in the absolute quantity of nitrogen present in the air. But the same cannot be said of the oxygen.

Although we have no means of even approximately estimating the temperature of the earth when it was in the liquid state, still it is more than probable that many of the oxygen compounds which now form the crust of the earth were built up from their constituents as the earth gradually cooled to the still extremely high temperatures at which the compounds of oxygen with silicon, calcium, hydrogen, &c., can exist. Experiment has shown that water is not only decomposed by the electric current, but also when raised to a very high temperature. If at any time the temperature of the earth was higher than that requisite to decompose water, its atmosphere must have contained, besides nitrogen and hydrogen, much larger quantities of oxygen than after it had cooled down. Only when the temperature fell low enough could the hydrogen and oxygen unite together with enormous explosions to form water vapour. Possibly the protuberances of the sun's atmosphere, which are considered to be chiefly glowing hydrogen, are produced by the union of immense quantities of hydrogen and oxygen at heights in the sun's atmosphere where the temperature is low enough to allow these two substances to combine with one another.

Whether the amount of carbonic acid present in the atmosphere was ever greater than is now the case, cannot be satisfactorily answered in the present state of our knowledge. We know that during geological time immense quantities of carbonic acid, as calcium carbonate (limestone), have become a portion of the solid crust of the earth. A further quantity of carbonic acid has also been fixed in the form of our deposits of coal, the remains of extinct plants. At the same time it must not be forgotten that the air is continually receiving carbonic acid from the interior of the earth by volcanoes, active and extinct, and how far these two processes balance one another we are at present unable to say. The luxuriant vegetation which produced our coal-fields seems to indicate that the amount of carbonic acid then present in the atmosphere was greater than now.

The quantity of oxygen contained in the atmosphere is proportionally small, and must be continually diminished by the respiration of men and animals and by the enormous quantities of coal which are continually being burnt. At the same time the quantity of carbonic acid in the air is increased by these processes. The question thus suggests itself, Can this enormous consumption of oxygen ever deprive the air of such quantities of this gas as to render respiration impossible? We know the quantity of oxygen which is daily consumed by a man, from which we can easily obtain the quantity of oxygen annually consumed by the entire human race (reckoned at 1,500,000,000); and we can further calculate the total quantity of oxygen contained in the air. Now, if we consider that the oxygen consumed by animals, processes of putrefaction and combustion, is even nine times more than that consumed by man, then in 1,800 years the total quantity of oxygen in the air would only be diminished by about one-fifth per cent. But the idea that the air can ever become too poor in oxygen for respiration may be discarded when we remember the action of green plants on atmospheric carbonic acid. Green plants require carbonic acid for their existence and growth as much as animals require oxygen; under the influence of sunlight their green parts decompose the carbonic acid, assimilating the carbon and setting the oxygen free. Thus, by the mutual action of plants and animals, the proportions of oxygen and carbonic acid in the air remain practically unchanged for a long time.

Water and air, once considered to be chemical elements, are still important elements in another sense, and especially for the

science of health. The remains of Roman aqueducts illustrate the importance which was attached to a good supply of pure water 2,000 years ago by a nation without our present scientific knowledge. But in this respect we are still far behind the Romans. For centuries we have contented ourselves with impure well-water, and only in recent years have cholera, typhus, and other epidemics, together with a general high death-rate, been attributed to an impure and insufficient water supply.

The question of ventilation, or the supply of pure fresh air, is even more neglected. It is well known how detrimental it is for a number of persons to remain long in a closed space where the air becomes charged with carbonic acid, water vapour, and other noxious emanations from the body, and it is also well known how easily this great evil may be avoided by leading away the bad air and supplying good air in its place. But, notwithstanding this knowledge, public and private buildings are continually being erected with insufficient ventilation, or, in some cases, with even none at all.

COMPOUNDS OF NITROGEN WITH THE HALOGENS.

Nitrogen combines with the halogens even less easily than with hydrogen, and never unites directly with them. The halogen compounds of nitrogen can only be obtained, like ammonia, by indirect methods; unlike ammonia, which they resemble in composition, they do not unite with acids, and they are further distinguished by their great instability.

The elements in these compounds are so loosely combined, that mere contact with some indifferent liquid or solid often suffices to decompose them with a powerful explosion. They are therefore dangerous substances to deal with, and their properties ought to be known before commencing experiments with them. The best known of these compounds are nitrogen chloride and nitrogen iodide.

Nitrogen Chloride : NCl_3 (?). This compound, which may be considered as ammonia in which the hydrogen is partly or entirely displaced by chlorine, but of which the exact composition is un-

known, is obtained by the action of free chlorine on ammonia, with simultaneous production of hydrochloric acid.

Nitrogen chloride is a yellow oily liquid, with a specific gravity of 1·6, and sinks in water. It possesses a powerful, piercing odour, by which minute quantities of it may be detected.

The compound is easily obtained by passing chlorine into a saturated solution of ammonium chloride at about 30°, when the following reaction probably takes place :—

$$NH_4Cl + 3Cl_2 = 4HCl + NCl_3.$$

Aqueous ammonia is even more easily decomposed than the chloride, but cannot be employed, as the nitrogen chloride is again decomposed by free ammonia.

Owing to the great danger in experimenting with nitrogen chloride, it is not advisable to prepare large quantities of it. By the following method, small quantities, sufficient to observe its odour and explosive properties, may be safely obtained.

In a strong leaden dish about eight inches wide and four inches deep is placed a second smaller dish, also of lead, and about three inches wide, and the large dish then filled to about two-thirds with a luke-warm saturated solution of ammonium chloride. A cylindrical glass jar is also filled with the same liquid, inverted in the dish and suspended by a wire just over the smaller dish. Chlorine gas is now led into the cylinder until the liquid is completely displaced, when the apparatus is allowed to stand quietly. As the liquid now gradually rises in the jar, small oily drops of nitrogen chloride appear on the surface, which gradually fall into the small leaden dish. When nearly all the chlorine is absorbed, the small dish is removed, a portion of the solution poured off, and the compound exploded. The explosion is best brought about by tying an oiled feather to the end of a long stick, and then bringing it into contact with the nitrogen chloride; the whole then instantly explodes, while the liquid is shot up several feet high and the base of the leaden dish pressed quite flat.

The force of the explosion is so great that a drop of the chloride of the size of a pea, exploded under water in a porcelain dish with an oiled feather, not only breaks the dish into small fragments, but forces the piece immediately under the drop into the wooden support.

The discoverer of nitrogen chloride, the French chemist Dulong, who, being unacquainted with its explosive character, attempted to

distil some in a retort, lost several fingers of one hand by the explosion.

If in any way larger quantities of nitrogen chloride have been obtained than it is considered advisable to explode, the substance may be left to itself under the liquid. After some little time, it will gradually disappear owing to spontaneous decomposition.

Nitrogen chloride is also obtained by the electrolytic decomposition of ammonium chloride. If two platinum plates are immersed in a warm saturated solution of the salt, and a strong current passed for a short time, the chlorine, which is evolved at the positive plate, becomes converted into nitrogen chloride. A powerful explosion then ensues if the two plates are brought into contact.

Nitrogen Iodide : NI_3 (?). This compound is a dark-brown solid, closely resembling precipitated iodine. It is obtained when a saturated alcoholic solution of iodine is mixed with excess of strong ammonia. The precipitate is then brought on a filter and well washed with water. As long as the substance is moist, it bears pressure and contact with all those substances which so easily explode nitrogen chloride ; but if dried, mere contact with a particle of dust or the percussion produced by closing a door is often sufficient to decompose it into its constituents with an explosion.

PHOSPHORUS.

Chemical Symbol : P.—*Atomic Weight* : 31.

Phosphorus is not found in the free state in nature, but occurs in the mineral kingdom principally as calcium phosphate in the minerals *phosphorite*, *apatite*, &c., and in *coprolites*. All soils contain phosphorus, but usually in only minute quantities. From the soil the phosphorus is taken up by plants, which produce very complex organic compounds containing it, and is collected by them in various parts of their structures, particularly in their seeds. These phosphorus compounds then pass into the bodies of animals with the nutriment contained in the plants ; they form an important constituent of the blood, nerve substance, &c., and undergo an oxidation in the body, being again converted into phosphoric acid

In combination with lime, this phosphoric acid forms the greater part of the mineral substance of the bones, while a portion is expelled from the body in the fæces, and a larger portion in the urine, and is thus returned again to the soil.

Phosphorus was first obtained by its discoverer, Brand, of Hamburg (1669), from concentrated urine. A hundred years later Scheele recognized the fact that bones as well as urine contain calcium phosphate, and that it is this substance which yields the phosphorus obtained from urine. The name phosphorus is derived from its property of shining in the dark (φῶς, light, and φέρειν, to bear).

We are acquainted with phosphorus in at least two different modifications, which are so different in appearance and in their physical as well as in some of their chemical properties that they might have been thought to be different elements if it were not easy to convert one into the other, and if the products of their union with other elements were not the same.

The variety longest known, and commonly called *ordinary* or *white* phosphorus, is, when freshly prepared, a colourless transparent solid, which is coloured yellow under the action of light, and has a specific gravity of 1·83. It may be melted under water at a temperature of 44° to a colourless liquid, easily solidifying again and sometimes assuming a crystalline form. At the ordinary temperature phosphorus is as soft as wax, but becomes brittle at low temperatures. Phosphorus boils at 290°, and when out of contact with air may be distilled unchanged. Its gas is colourless, and has a specific gravity (at 1,000°) of 4·5. From the density of its vapour its molecular weight is $4·5 \times 28·88 = 129·9$, or, in other words, the molecule of phosphorus in the gaseous state has the composition P_4 and contains four atoms.

Phosphorus heated in the air slightly above its melting point catches fire and burns, producing white fumes of phosphoric anhydride. At lower temperatures, when exposed to the air it oxidizes without the production of flame, forming phosphorous anhydride. The white fumes produced when a stick of phosphorus is exposed to the air, and which are luminous in the dark, are due to phosphorous anhydride, and the garlic like odour noticed at the same time is produced by the same substance. Ordinary phosphorus is so inflammable that it catches fire when rubbed on a rough surface; it should never be held, even for a short time, between the fingers, as burning phosphorus produces very painful,

slowly healing wounds. This modification of phosphorus is always preserved under water, in which it is insoluble. And although it possesses a very strong affinity for oxygen, it does not decompose water like potassium and sodium. It is slightly soluble in alcohol and ether, but easily soluble in carbon disulphide, from which solution it again separates in crystals belonging to the regular system. Phosphorus in this modification is extremely poisonous; even small quantities have been known to produce fatal effects.

A second modification of phosphorus is the *red* or *amorphous* variety. This is a red-brown amorphous powder, of specific gravity 2·2 (or heavier than common phosphorus). It does not melt, even when heated up to 250°, neither does it produce white fumes when exposed to the air, nor is it luminous in the dark. It catches fire in the air only when heated up to 260°, is insoluble in carbon disulphide, is odourless, and not poisonous.

This red modification is produced when ordinary phosphorus is heated in an atmosphere of carbonic acid or hydrogen to a temperature of 240° for some time; the change goes on more quickly if the phosphorus is heated in sealed tubes to 300°. But in all cases the weight of the phosphorus neither increases nor diminishes. If iodine is mixed with an excess of ordinary phosphorus and the mixture heated, the portion of phosphorus which does not combine with the iodine is converted into the red variety. A small quantity of iodine suffices to produce the change in a large quantity of phosphorus. The same change is also slowly produced by the action of light. Phosphorus exposed to the light becomes first yellow and then red. In order to purify the red modification from common phosphorus mechanically mixed with it, it may be repeatedly shaken with carbon disulphide or boiled with caustic soda.

It is remarkable that just as ordinary phosphorus is converted into the red variety on heating, so also the latter may be changed into the former by the action of heat. Amorphous phosphorus heated in a retort filled with carbonic acid to 260°—*i.e.* to a temperature only slightly higher than is required for its production —is completely changed into the common form. And in this case, too, no change in weight is observed.

Since phosphorus has been employed for important technical purposes, particularly for the manufacture of lucifer matches, large quantities are annually manufactured. The material employed for its extraction is not urine, from which it was first prepared, but is the calcium phosphate of burnt bones, or as one of the several

forms in which the compound occurs in the mineral kingdom. Although the attraction of phosphorus for oxygen is very great, it is exceeded by that of glowing charcoal. Phosphoric acid, in the proper form, when mixed with powdered charcoal and heated to bright redness, is completely reduced with formation of carbonic oxide. But if the compound of phosphoric acid and lime, as it occurs in nature or in burnt bones (calcium phosphate, $Ca_3(PO_4)_2$), were employed, no reduction would take place. It is only the free acid, or compounds of calcium containing more phosphoric acid than the normal salt, which are decomposed on heating with charcoal. In order to obtain such a compound the following method is adopted. Finely powdered bone-ash, containing normal calcium phosphate, is warmed with enough dilute sulphuric acid to withdraw two-thirds of the calcium, which unites with the sulphuric acid forming insoluble sulphate, while the remaining third of the calcium remains combined with the whole of the phosphoric acid as a soluble acid phosphate: $H_4Ca(PO_4)_2$, or $\left.\begin{matrix}PO\\PO\end{matrix}\right\}\begin{matrix}(OH)_4\\O_2Ca\end{matrix}$, commonly called *superphosphate of lime*:—

$$\left.\begin{matrix}PO\\PO\end{matrix}\right\}O_6Ca_3 + 2SO_2(OH)_2 = 2SO_2\cdot O_2Ca + \left.\begin{matrix}PO\\PO\end{matrix}\right\}\begin{matrix}(OH)_4\\O_2Ca\end{matrix}$$

The clear solution is next drawn off and concentrated in leaden pans, and the concentrated solution so obtained is then mixed with powdered charcoal, dried, and heated to low redness. During this process the acid phosphate loses water and becomes converted into calcium metaphosphate: $Ca(PO_3)_2$, or $\left.\begin{matrix}PO_2\\PO_2\end{matrix}\right\}O_2Ca$, a compound which contains more phosphoric acid than the normal phosphate, and from which two-thirds of the phosphorus is obtained on glowing with charcoal:—

$$3(PO_2)_2O_2Ca + 10C = P_4 + \left.\begin{matrix}PO\\PO\end{matrix}\right\}O_6Ca_3 + 10CO,$$

the calcium being reconverted into normal phosphate. (See App.) The reduction is carried on in earthenware retorts connected with earthenware vessels containing water. The gaseous phosphorus distils over and condenses under the water, while the carbonic oxide escapes. The raw product is then purified by redistillation from iron retorts and by squeezing the liquid through leather under warm water. Phosphorus as it occurs in trade is usually

in the form of sticks; this form is given it by the highly dangerous practice of sucking up the molten substance under water into conical glass tubes, from which it is easily removed on solidification. (See Appendix.)

If a stick of phosphorus, one end of which is wrapped in paper, is used to write on a board, the characters are luminous in the dark. Small pieces of phosphorus are by this means rubbed off on the board and gradually oxidize to phosphorous acid. The luminosity of phosphorus or its oxidation to phosphorous acid is always accompanied with the production of ozone. Various bodies in the gaseous state when mixed with atmospheric air prevent its slow oxidation and at the same time its luminosity; among these are small quantities of oil of turpentine vapour, ether, ammonia, and various hydrocarbons. Phosphorus is, however, much less luminous in pure oxygen than in common air, or in oxygen diluted with an indifferent gas.

Phosphorus unites as easily with the halogens as with oxygen, liberating a large amount of light and heat. With chlorine it forms either phosphorus trichloride or pentachloride according to the relative quantities of phosphorus and chlorine which act upon one another.

The affinity of phosphorus for sulphur is so great that by dropping flowers of sulphur on to phosphorus melted under water the union takes place with a very considerable elevation of temperature, and dangerous explosions may often be produced. Phosphorus does not appear to unite directly with hydrogen, nitrogen, or carbon.

The principal use of phosphorus is in the manufacture of lucifer matches, for which both modifications are employed. Common matches are dipped in a mixture containing common phosphorus and ignite when rubbed on any rough surface, the ignition being imparted to the wood by previously dipping the matches in melted paraffin. In the other kind of matches, commonly known as *safety matches*, the matches themselves contain no phosphorus but only some substance which readily gives off oxygen (usually potassium chlorate), while one side of the box is covered with finely divided amorphous phosphorus put on with gum water. The matches are then ignited by rubbing them on the prepared surface. Their ignition is due to the change of the part of the amorphous phosphorus rubbed by the match into the common form by the heat of friction; this then adheres to the match and causes it

catch fire. If phosphorus is rubbed up with fat a mixture is produced which is luminous in the dark, and which is used as a poison for rats and mice.

COMPOUNDS OF PHOSPHORUS WITH HYDROGEN.

Three compounds of these elements are known—viz. a gaseous compound having the composition PH_3, and corresponding to ammonia (NH_3), a liquid, P_2H_4, corresponding to hydrazine (N_2H_4), and a solid, P_4H_2, the nitrogen analogue of which is not yet known.

Gaseous Phosphoretted Hydrogen or Phosphine: PH_3.

This compound is a colourless gas, with an exceedingly unpleasant garlic odour, and is nearly insoluble in water. Its specific gravity is 1·18, which corresponds to a molecular weight of 1·18 + 28·88 = 34·08, and its molecule is therefore represented by the formula PH_3.

The gas is not spontaneously inflammable, but at once ignites when brought into contact with a flame, burning to form water and phosphoric acid.

Phosphine is easily obtained by heating phosphorus with a solution of a strong base, such as potash, soda, lime, or baryta. Although phosphorus possesses so strong an attraction for oxygen it cannot decompose water even at the boiling temperature, but the decomposition goes on readily in the presence of a strong soluble base, a portion of the phosphorus uniting with the base to form a hypophosphite. The gas may also be prepared from solid calcium phosphide, which, in contact with warm water, is rapidly decomposed into phosphine, calcium hypophosphite, and calcium hydrate. But the gas obtained by either of these processes is always spontaneously inflammable. This is due to the fact that it contains small quantities of the volatile liquid phosphoretted hydrogen, which is spontaneously inflammable, and causes the gas to ignite in the air just as it does when mixed with other inflammable gases, such as carbonic oxide or hydrogen. The following equations represent the simultaneous production of the two compounds when phosphorus is heated with caustic potash :—

(i.) $4P + 3KOH + 3H_2O = 3H_2PO \cdot OK + PH_3$
Potassium hypophosphite

(ii.) $6P + 4KOH + 4H_2O = 4H_2PO \cdot OK + P_2H_4$.

The preparation of phosphine containing the spontaneously inflammable liquid compound must be performed with care. If phosphorus were heated in a flask half filled with caustic potash and provided with a tightly fitting cork and delivery-tube, the phosphoretted hydrogen would unite with the oxygen in the flask and catch fire, and the heat so produced would be sufficient to cause an explosion. It is better, therefore, to fill the flask nearly up to the neck and to place the cork in loosely until the oxygen contained in the small quantity of air present has been consumed. The delivery-tube must be wide so that it may not become closed with small particles of phosphorus carried over mechanically; it should dip under warm water.

In order to prepare the spontaneously inflammable gas from calcium phosphide, this compound is broken into small pieces of the size of a pea and dropped through a wide tube into a Woulffe's bottle half filled with warm water, the other tubulus of the bottle being provided with a delivery tube. The wide tube must just dip under the liquid and must be closed with a small cork. Before any calcium phosphide is introduced, the air contained in the Woulffe's bottle must be completely displaced by carbonic acid to prevent the gas from catching fire inside the bottle.

The spontaneously inflammable gas when preserved over water for some time, and particularly when exposed to the light, is found to lose its property of catching fire when brought into contact with the air, and at the same time the walls of the glass vessel become covered with a yellow film. This phenomenon depends upon the instability of the liquid compound, which easily breaks up, especially in sunlight, into gaseous and solid phosphines:—

$$5P_2H_4 = 6PH_3 + P_4H_2.$$

The said yellow film is found to contain phosphorus and hydrogen in the proportion necessary for the formula P_4H_2. The spontaneously inflammable liquid may be easily separated from the gaseous compound by passing the mixture through a U-tube placed in a freezing mixture. By this means the volatile liquid is condensed and the gas is no longer spontaneously inflammable, but takes fire when heated to a temperature above 100°.

Pure phosphine may be prepared by dropping calcium phos

phide into hydrochloric acid instead of into water, or by acting upon phosphorus with alcoholic instead of aqueous caustic potash. Hydrochloric acid and alcohol appear to prevent the formation of the liquid phosphoretted hydrogen, or to decompose it immediately.

The pure gas when led into nitric acid mixed with a small quantity of the fuming acid becomes spontaneously inflammable. This is probably due to the abstraction of a portion of its hydrogen, which is oxidized by the nitric acid, with the production of liquid phosphoretted hydrogen.

Phosphine is distinguished from its analogue ammonia not only by its insolubility in water, but also by its incapability of uniting either with hydrochloric acid or with oxy-acids to form chemical compounds, but it still possesses weak basic properties. If dry phosphine and dry hydriodic acid are brought into contact with one another they unite to form a compound called *phosphonium iodide*, PH_4I (p. 128), analogous in composition to ammonium iodide, which crystallizes in cubes, and may be sublimed unchanged. The compound is, however, unstable; it is decomposed by water into hydriodic acid and phosphine.

Liquid Phosphoretted Hydrogen: P_2H_4.

This compound, which is prepared from the spontaneously inflammable gas by passing it through a freezing mixture, is a colourless, powerfully refractive liquid, does not mix with water, and at once catches fire when exposed to the air. The liquid undergoes a gradual decomposition, even in sealed tubes, into phosphines. The gas finally exercises so great a pressure on the tube as to produce an explosion. It is, therefore, not practicable to preserve the liquid in sealed tubes. Under a pressure of 735 mm. it boils at 57°–58.°

Solid Phosphoretted Hydrogen: P_4H_2.

A reddish yellow mass formed, as above described, by the decomposition of the liquid phosphine. The decomposition is accelerated if concentrated hydrochloric acid be added. The solid phosphine does not burn unless heated to 160°.

OXIDES AND OXY-ACIDS OF PHOSPHORUS.

Although phosphorus is so closely allied to nitrogen, we are only acquainted with two oxides of this element—viz. phosphorous anhydride (P_4O_6) and phosphoric anhydride (P_2O_5), corresponding

to nitrous anhydride and nitric anhydride respectively. Compounds of phosphorus having a similar composition to nitric peroxide, nitric oxide, and nitrous oxide, have not yet been prepared. (See App.)

From these two oxygen compounds are derived the two acids, common tribasic phosphoric acid and dibasic phosphorous acid. Besides these, a third (lower) acid is also known, which is called hypophosphorous acid and is monobasic. The following are the formulæ of these three acids of phosphorus, all containing pentad phosphorus :—

Common phosphoric acid . . . $PO\begin{cases}OH\\OH\\OH\end{cases}$

Phosphorous acid . . . . $HPO\begin{cases}OH\\OH\end{cases}$

Hypophosphorous acid . . . $H_2PO{\cdot}OH$

A fourth acid of phosphorus has recently been discovered of the composition : $\begin{cases}PO(OH)_2\\PO(OH)_2\end{cases}$, and called hypophosphoric acid.

PHOSPHORIC ANHYDRIDE : P_2O_5.

The white fumes produced when phosphorus burns with a flame in dry air consist of this compound. If the phosphorus is burnt in a closed space—*e.g.* under a bell-jar—they then condense to a light snow-white powder, which very readily attracts moisture from the air and forms liquid phosphoric acid. When thrown into water the anhydride hisses like a red-hot iron, and a large quantity of heat is at the same time set free. In fact, there are few substances which equal this body in its attraction for water. Unlike nitric anhydride, it is not volatile at ordinary temperatures, and does not, therefore, fume in moist air ; but it may be sublimed when strongly heated in a glass tube.

The acid first produced when the anhydride unites with water contains only one atom of hydrogen displaceable by a metal, and is therefore monobasic. This acid is *metaphosphoric acid* : $PO_2{\cdot}OH$, and its production is shown by the following equation :—

$$\underset{\text{Phosphoric anhydride}}{\left.\begin{matrix}PO_2\\PO_2\end{matrix}\right\}O} + H_2O = \underset{\text{Metaphosphoric acid}}{2PO_2{\cdot}OH.}$$

Besides this phosphoric acid, which corresponds to nitric acid in its composition, we are also acquainted with a tri- and a tetrabasic acid. Tribasic phosphoric acid, which has the composition $PO(HO)_3$, and whose normal salts with monobasic metals contain three atoms of the metal replacing the three atoms of hydrogen, is *common* or *orthophosphoric acid.* Only compounds of this tribasic acid occur in nature.

Metaphosphoric acid, produced as we have seen from phosphoric anhydride and water, takes up a molecule of water when boiled and becomes converted into common phosphoric acid :—

$$PO_2{\cdot}OH \quad + \quad H_2O \quad = \quad PO(OH)_3.$$

The change which has taken place may be readily proved by a few simple reactions. Metaphosphoric acid coagulates white of egg, common phosphoric acid does not ; on adding a little ammonia, the former gives with silver nitrate a white precipitate of silver metaphosphate : $PO_2{\cdot}OAg$, the latter with the same reagent gives a yellow precipitate of silver orthophosphate : $PO(OAg)_3$. The conversion of metaphosphoric acid into common phosphoric acid is therefore complete when the liquid no longer coagulates white of egg and gives a bright yellow precipitate with silver nitrate.

Preceding the formation of common phosphoric acid from metaphosphoric acid, when the solution is warmed, is the production of *pyrophosphoric acid* (see App.), which may be recognized by the fact that this acid does not coagulate white of egg but gives a white precipitate of silver pyrophosphate when mixed with silver nitrate. Its production from the monobasic acid is shown by the following equation :—

$$\underset{\text{Metaphosphoric acid}}{2PO_2{\cdot}OH} \quad + \quad H_2O \quad = \quad \underset{\text{Pyrophosphoric acid}}{O\begin{cases}PO(OH)_2\\PO(OH)_2\end{cases}}$$

All three acids may therefore be represented as compounds of phosphoric anhydride with varying quantities of water, thus :—

$$\left.\begin{matrix}PO_2\\PO_2\end{matrix}\right\}O \quad + \quad H_2O \quad = \quad \underset{\text{Metaphosphoric acid}}{2PO_2OH}$$

$$\left.\begin{matrix}PO_2\\PO_2\end{matrix}\right\}O \quad + \quad 2H_2O \quad = \quad \underset{\text{Pyrophosphoric acid}}{O\begin{cases}PO(OH)_2\\PO(OH)_2\end{cases}}$$

$$\left.\begin{matrix}PO_2\\PO_2\end{matrix}\right\}O \quad + \quad 3H_2O \quad = \quad \underset{\text{Orthophosphoric acid}}{2PO(OH)_3}$$

ORTHO- OR COMMON PHOSPHORIC ACID: $PO(OH)_3$

On evaporating the aqueous solution of common phosphoric acid, when the temperature is not allowed to rise much above 150°, the acid remains behind as a colourless, thick, viscid liquid, of specific gravity 1·88, from which large, colourless crystals occasionally separate out. It readily attracts moisture from the air and deliquesces. When heated more strongly it loses water and becomes first converted into pyro- and then into metaphosphoric acid.

Common phosphoric acid is easily prepared by oxidizing phosphorus with nitric acid. Sticks of phosphorus are heated in a retort with pure nitric acid of specific gravity 1·2, when an energetic reaction takes place and red vapours of the lower oxides of nitrogen are given off. The retort is best provided with a cooled receiver, so that the nitric acid distilling over may be poured back into the retort. As soon as all the phosphorus has disappeared the excess of nitric acid is driven off, which at the same time oxidizes the phosphorous acid, also present, to the higher phosphoric acid. Finally, the viscid liquid is heated in a platinum dish until the temperature reaches 150°.

Another and very easy method of preparing phosphoric acid is from phosphorus pentachloride. If this substance is dropped into water in small quantities at a time, it decomposes, with considerable rise in temperature, into phosphoric and hydrochloric acids, phosphoric oxychloride being produced as an intermediate product:—

$$PCl_5 \quad + \quad 4H_2O \quad = \quad PO(OH)_3 \quad + \quad 5HCl.$$

Pure phosphoric acid may then be obtained by evaporating the strongly acid liquid.

Since commercial phosphorus always contains arsenic, because the sulphuric acid used in the preparation of the acid calcium phosphate is always contaminated with arsenic, the phosphoric acid prepared either from phosphorus or from phosphorus pentachloride always contains traces of arsenic in the form of arsenic acid. In order to separate this impurity the phosphoric acid, after being freed from the nitric or hydrochloric acid, is diluted with a large quantity of water, gently warmed, and a stream of sulphuretted hydrogen passed through it as long as insoluble yellow arsenious sulphide separates out. The whole of the arsenic is

precipitated, when a small portion of the clear liquid again saturated with sulphuretted hydrogen and allowed to stand for some hours shows no further turbidity. The clear filtered liquid then yields pure phosphoric acid on evaporation.

Phosphoric acid may also be prepared from the acid calcium phosphate (superphosphate of lime), obtained by acting on bone-ash or some other form of calcium phosphate with sulphuric acid. The solution of the superphosphate, which still contains calcium sulphate, is mixed with a solution of ammonium carbonate to precipitate the lime. The filtered liquid, which contains ammonium sulphate and phosphate, is then evaporated to dryness and glowed in order to drive off the ammonium sulphate and to expel the ammonia from the ammonium phosphate. Phosphoric acid prepared in this way always contains, however, small quantities of ammonium salts. (See Appendix.)

Phosphoric acid is one of the strongest inorganic acids. At a high temperature it even expels sulphuric acid from its compounds, being less volatile than this acid. Since it is a tribasic acid, it forms three series of salts :—

(i.) *Normal salts*, in which all *three* of its hydrogen atoms are displaced by a metal.

(ii.) *Monacid salts*, in which *two* atoms of hydrogen are displaced by a metal, and (iii.) *Diacid salts*, in which only *one* atom of hydrogen is displaced.

In the normal salts the hydrogen may be either displaced by three atoms of a monad metal, by one of a monad and one of a diad or, by one of triad metal, thus :—

Normal sodium phosphate . . .	$PO(ONa)_3$
Normal sodium-ammonium phosphate .	$PO\begin{cases}(ONa)_2\\ONH_4\end{cases}$
Normal ammonium-magnesium phosphate	$PO\begin{cases}O_2Mg''\\ONH_4\end{cases}$
Normal ferric phosphate	$PO{\cdot}O_3Fe'''$

In the first class of acid salts the two atoms of hydrogen may either be displaced by two atoms of a monad metal or by one atom of a diad, thus :—

Monacid sodium phosphate . . .	$PO\begin{cases}(ONa)_2\\OH\end{cases}$
Monacid calcium phosphate . . .	$PO\begin{cases}O_2Ca'\\OH\end{cases}$

And, finally, for the second class of acid salts we may take as an example. —

Diacid sodium phosphate . . . . . $PO\begin{cases}ONa\\(OH)_2\end{cases}$

The phosphates of the metals, particularly the normal salts, are mostly insoluble in water, but easily soluble in nitric acid; only the phosphates of the alkalies can be obtained in a well-defined crystalline state from their solutions.

Normal silver phosphate is a bright yellow amorphous precipitate, easily soluble in nitric acid. It is obtained on the addition of silver nitrate to a solution of common sodium phosphate. This latter compound, the *phosphate of soda* of the shops, is not the normal compound, but is monacid sodium phosphate—*i.e.* it contains one atom of hydrogen undisplaced. The reaction by which normal silver phosphate is produced when this salt is mixed with silver nitrate is as follows:—

$$PO\begin{cases}(ONa)_2\\OH\end{cases} + 3NO_2\cdot OAg = PO(OAg)_3 + 2NO_2\cdot ONa + NO_2OH.$$

Whence it is seen that nitric acid is at the same time set free, and if the clear liquid is filtered off, it will be found to possess an acid reaction, and to contain some silver phosphate dissolved in it. We produce, therefore, from the two neutral solutions of monohydric sodium phosphate and silver nitrate an acid liquid. The phosphoric acid contained in this and other similar acid compounds can, therefore, only be completely precipitated by silver nitrate by neutralizing with soda or some other suitable base.

The insolubility of ammonium-magnesium phosphate in water, especially in presence of ammonia, and the constant composition of this compound, makes it well adapted both to detect phosphoric acid and to determine its quantity. It is precipitated as a white crystalline powder when a solution of sodium or any other soluble phosphate is mixed with magnesium sulphate, ammonium chloride, and ammonia.

If monacid sodium phosphate is mixed with magnesium sulphate the acid magnesium compound is produced. Thus:—

$$PO\begin{cases}(ONa)_2\\OH\end{cases} + SO_2\cdot O_2Mg = PO\begin{cases}O_2Mg\\OH\end{cases} + SO_2\cdot(ONa)_2,$$

which is soluble in water, even in the presence of ammonium chloride If, however, ammonia is added in excess, the insoluble ammonium magnesium phosphate is precipitated:—

$$PO\begin{cases}O_2Mg\\OH\end{cases} + NH_3 = PO\begin{cases}O_2Mg\\ONH_4\end{cases}$$

The addition of ammonium chloride is necessary to prevent the precipitation of magnesium hydrate from the excess of magnesium sulphate and ammonia. Magnesium hydrate forms an easily soluble compound with ammonium chloride.

An excellent method of detecting and separating phosphoric acid in nitric acid solutions containing iron, lime, &c., is furnished by molybdic acid. If such a solution containing free nitric acid is mixed with a solution of ammonium molybdate in nitric acid, the liquid first becomes yellow and then deposits a yellow crystalline precipitate consisting of a compound of phosphoric and molybdic acids. By this means a soil, for example, may be examined for phosphoric acid, and its quantity, if present, determined.

If solid monacid sodium phosphate is gently heated, it first of all loses its water of crystallization. On further heating it gives up the hydrogen which it contains, together with sufficient oxygen to form water, and normal sodium pyrophosphate remains behind:—

$$2PO\begin{cases}(ONa)_2\\OH\end{cases} = O\begin{cases}PO(ONa)_2\\PO(ONa)_2\end{cases} + H_2O.$$

When diacid sodium phosphate is heated, water is also given off, but the compound which remains behind is then normal sodium metaphosphate:—

$$PO\begin{cases}ONa\\(OH)_2\end{cases} = PO_2\cdot ONa + H_2O.$$

The same compound is more easily obtained by heating acid ammonium-sodium phosphate (*microcosmic salt*), which then gives off ammonia and water:—

$$PO\begin{cases}ONa\\ONH_4\\OH\end{cases} = PO_2\cdot ONa + NH_3 + H_2O.$$

Pyrophosphoric Acid: $O\begin{cases}PO(OH)_2\\PO(OH)_2\end{cases} = H_4P_2O_7.$

This compound is obtained as a colourless crystalline mass, easily soluble in water, when phosphoric acid is heated slightly above 200°, until a portion when neutralized with ammonia gives a pure white precipitate with silver nitrate. If sodium pyrophosphate, obtained as mentioned above, is dissolved in water mixed

with silver nitrate, the white precipitate filtered off, washed well, and then again decomposed by passing a current of sulphuretted hydrogen through water containing it in suspension, black silver sulphide is formed, and the acid solution contains pyrophosphoric acid. Such an aqueous solution of the acid cannot, however, be kept for any time; it combines with water and forms common phosphoric acid, slowly when cold, more rapidly when heated :—

$$O\begin{cases}PO(OH)_2\\PO(OH)_2\end{cases} + H_2O = 2PO(OH)_3.$$

Pyrophosphoric acid is a tetrabasic acid, its four atoms of hydrogen may be displaced by the same or by different metals, and besides the normal salts three classes of acid salts are also known accordingly as one, two, or three atoms of hydrogen are displaced.

Metaphosphoric Acid : $PO_2\cdot OH$.

This acid is obtained in aqueous solution by allowing phosphoric anhydride to deliquesce in the air, or as a vitreous, amorphous mass by heating common phosphoric acid to redness. In the latter state it forms the *glacial phosphoric acid* of the pharmacists. In combination with sodium it is produced, as we have already seen, by heating microcosmic salt to redness.

The acid and its soluble salts give with silver nitrate an insoluble white precipitate of silver metaphosphate : $PO_2\cdot OAg$, and are distinguished from the two other phosphoric acids and their salts by their property of coagulating albumen (white of egg).

Metaphosphoric acid when in solution gradually absorbs water and is converted into common phosphoric acid. The change goes on slowly in the cold, but more rapidly when the liquid is heated. Solutions of the metaphosphates also take up water in the same way—*e.g.* :—

$$PO_2\cdot ONa + H_2O = PO\begin{cases}ONa\\(OH)_2\end{cases}.$$

The recently discovered *hypophosphoric acid* : $\begin{cases}PO(OH)_2\\PO(OH)_2\end{cases}$, is a tetrabasic acid intermediate between phosphoric and phosphorous acids, and is produced with phosphorous and phosphoric acids, when phosphorus oxidizes slowly in moist air. Its solution may be evaporated at a low temperature, but is decomposed on boiling into phosphorous and phosphoric acids. (See Appendix.)

Phosphorous Anhydride: P_4O_6

The white fumes produced when a stick of phosphorus is exposed to the air consist principally of phosphorous acid. The pure anhydride may be obtained by gently heating a stick of dry phosphorus in a glass tube and leading a current of dry air over it. The phosphorus then burns with a pale greenish flame, and the anhydride is deposited in the cool end of the tube as a snow-white powder resembling phosphoric anhydride. Phosphorous anhydride has still a strong attraction for oxygen; when exposed to the air it catches fire and burns to phosphoric anhydride.

When phosphorous anhydride is brought into contact with water, or when phosphorus is allowed to oxidize slowly in moist air, the corresponding acid—phosphorous acid—is produced.

Phosphorous Acid: $HPO\begin{cases}OH\\OH\end{cases}$

Although this compound contains three atoms of hydrogen, only two of them can be displaced by metal, and it is therefore a dibasic acid. It is best prepared by dropping phosphorus trichloride into water. The chloride then breaks into hydrochloric and phosphorous acids, thus:—

$$PCl_3 + 3H_2O = 3HCl + HPO\begin{cases}OH\\OH\end{cases}$$

The strongly acid liquid is freed from the hydrochloric acid by rapid evaporation, when phosphorous acid remains behind as a clear, colourless syrup, which if preserved for some time over sulphuric acid in a vacuum changes into a crystalline mass.

Pure phosphorous acid is obtained as a bye-product in the preparation of acetyl chloride, when glacial acetic acid is gradually added to phosphorus trichloride, contained in a retort, and the volatile acetyl chloride together with the excess of acetic acid distilled off. Phosphorous acid then remains behind as a thick colourless liquid, which solidifies on cooling. If we represent the radical of acetic acid by the symbol $\bar{A}$, acetic acid then has the formula $\bar{A}OH$, and the process is represented by the following equation:—

$$PCl_3 + 3\bar{A}OH = 3\bar{A}Cl + HPO(OH)_2.$$

Phosphorous acid melts at 70°; if the acid is strongly heated it

breaks up into phosphoric acid and phosphine, the latter catching fire in the air :—

$$4HPO(OH)_2 = 3PO\cdot(OH)_3 + PH_3.$$

The phosphites when strongly heated undergo a similar change.

The strong attraction of phosphorous acid for oxygen and its readiness to pass into phosphoric makes it a powerful reducing agent. When an aqueous solution is gently warmed with solutions of mercury or silver the compounds of these metals are reduced to the metallic state. Similarly, when the acid is exposed to the air it gradually takes up oxygen and becomes converted into phosphoric acid.

Hypophosphorous Acid : $(H_2PO)OH$.

This acid of phosphorus, which contains less oxygen than phosphorous acid, is monobasic. Its molecule contains three atoms of hydrogen, but only one of these atoms can be displaced by a metal. The acid is soluble in water, and on evaporating down its aqueous solution remains behind as a syrupy liquid, which crystallizes below 0°. Most of its salts crystallize easily, and are all soluble in water.

The hypophosphites are produced, as we have already seen (p. 211), when an aqueous solution of an alkali is heated with phosphorus. Phosphoretted hydrogen is then evolved, and the hypophosphite remains behind in solution. For the preparation of hypophosphorous acid and its salts it is best to employ barium hydrate (baryta-water), since the insolubility of barium carbonate affords a ready means of removing the excess of alkali. After a hot saturated solution of baryta-water has been heated with excess of phosphorus for some time until phosphoretted hydrogen is no longer evolved, the whole is allowed to cool, and carbonic acid passed through the clear liquid until it no longer reacts alkaline ; heat being applied towards the end. The barium carbonate is then filtered off, and the liquid evaporated down, when barium hypophosphite crystallizes out on cooling. The production of this salt is represented by the following equation, which is similar to that by which potassium hypophosphite is formed (p. 212) :—

$$6P + 2Ba(OH)_2 + 4H_2O = 2\left.\begin{matrix}H_2PO\\H_2PO\end{matrix}\right\}O_2Ba'' + P_2H_4.$$

Milk of lime (calcium hydrate) may be employed instead of the baryta-water, when calcium hypophosphite is easily obtained in the crystalline form. Calcium hypophosphite is also obtained when calcium phosphide is decomposed by warm water (p. 211).

The free acid may be prepared from the barium salt by precipitating the barium with sulphuric acid and filtering off from the insoluble barium sulphate. The aqueous solution can be evaporated to a certain degree of concentration without decomposition, but when more strongly heated breaks up (like phosphorous acid) into phosphoric acid and phosphine :—

$$2H_2PO \cdot OH = PO(OH)_3 + PH_3.$$

It possesses a strong attraction for oxygen, and, like phosphorous acid, reduces various metals from their oxides or from solutions of their salts.

COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS.

We are acquainted with two compounds of phosphorus and chlorine—viz. phosphorus trichloride, PCl_3, in which the phosphorus is triad, and phosphorus pentachloride, PCl_5, in which the phosphorus is pentad. Similar compounds with bromine are also known. A corresponding phosphorus triodide, PI_3, also exists, but the pentaiodide has not been prepared ; on the other hand, a compound containing less iodine, of the composition $(PI_2)_2$ or P_2I_4—phosphorus di-iodide—is known. Phosphorus forms only one compound with fluorine—the gaseous pentafluoride, PF_5.

The attraction between phosphorus and the halogens is so great that all these compounds, except the fluoride, can be easily prepared by the direct union of their constituents ; while the strong attraction of phosphorus for oxygen and of the halogens for hydrogen is the reason why these compounds are easily decomposed by water with a considerable evolution of heat.

PHOSPHORUS TRICHLORIDE (**Phosphorous Chloride**).

Composition: PCl_3.

This compound is a colourless liquid, fuming in moist air, and which may be prepared in quantity in the following manner. The bottom of a large tubulated retort is covered about half an inch deep with dry sand, and when the air has been expelled by carbonic acid carefully dried sticks of phosphorus are introduced. The neck of the retort is then connected with a cooled receiver, and a rapid stream of dry chlorine led into it. The phosphorus catches fire in the atmosphere of chlorine, melts, and burns with a pale flame, forming the trichloride which distils over. The process must be so regulated that the chlorine is not in excess, partly by reducing the current of the gas and partly by heating the retort more strongly. An excess of chlorine would produce the solid pentachloride. But if too much phosphorus vapour is produced, a portion distils over into the condenser and receiver. In the preparation of large quantities it is best to employ several vessels generating chlorine, when the trichloride can then be distilled in an even stream.

The substance so obtained is never pure; either it contains dissolved pentachloride or free suspended phosphorus. In the latter case redistillation is sufficient to remove most of the phosphorus: in the former case the liquid must be digested with free phosphorus, which converts the pentachloride into the trichloride, and be again distilled. The phosphorus trichloride then only contains small quantities of free dissolved phosphorus, for which it is a good solvent.

Phosphorus trichloride is a clear, colourless liquid of 1·58 specific gravity. It boils at 76°, and its vapour has a density of 4·7, which corresponds to a molecular weight of 137, and its composition PCl_3. It fumes in moist air and is at once decomposed by water into phosphorous and hydrochloric acids with a considerable rise in temperature. With chlorine it unites readily and forms the solid pentachloride.

PHOSPHORUS PENTACHLORIDE (Phosphoric Chloride).

Composition: PCl_5.

The solid volatile phosphorus pentachloride is easily prepared from the liquid trichloride by causing the latter to unite directly with two further atoms of chlorine. A wide-necked flask is about half filled with phosphorus trichloride on to which chlorine is led by a wide tube passing through a glass plate closing the neck of the flask. The tube must not touch the liquid or it will become closed by the solid pentachloride. The chlorine is rapidly absorbed, a large quantity of heat is evolved, and the flask must be kept cool throughout the operation. It is necessary to stir the mass from time to time and finally to slightly warm it. The conversion is complete when chlorine is no longer absorbed on allowing the solid mass to stand in contact with the gas in closed vessels.

Another method of preparation consists in dissolving phosphorus in carbon disulphide, and then passing chlorine through this solution. Phosphorus pentachloride, which is insoluble in carbon disulphide, then separates out in indistinct crystals.

Phosphorus pentachloride is a white crystalline mass fuming in the air. It sublimes without melting at 100°, and melts under pressure at about 148.° Its vapour when inhaled is exceedingly irritating, a fact which should not be forgotten in experimenting with it. All operations with it should be carried on in a good draught of air. Its vapour density is 3·6, corresponding to a molecular weight of 104, which is only one-half that required for the formula PCl_5 (208·5). The reason of this is that one molecule of the pentachloride breaks up when heated (dissociates) into one molecule of the trichloride and one of free chlorine, which occupy twice the volume that one molecule of the pentachloride would take up. On cooling again the two substances recombine and produce phosphorus pentachloride. When the pentachloride is thrown into water it is at once decomposed with a large evolution of heat, while a colourless oil collects at the bottom of the vessel and after a time disappears. This oil is phosphoric oxychloride,

$POCl_3$, or the chloride of common phosphoric acid, $PO(OH)_3$. It is decomposed by water into phosphoric and hydrochloric acids:—

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$
$$POCl_3 + 3H_2O = PO \cdot (OH)_3 + 3HCl.$$

The tendency of phosphorus pentachloride to exchange two atoms of chlorine for one of oxygen makes it a valuable agent for preparing compounds of chlorine which are difficult to obtain in any other way. We have seen (p. 165) that when a mixture of phosphorus pentachloride and sulphuric acid is heated, chlorsulphonic acid, phosphoric oxychloride, and hydrochloric acid are formed.

PHOSPHORIC OXYCHLORIDE (**Phosphoryl Chloride**).

Composition: $POCl_3$.

This substance, which closely resembles phosphorus trichloride in its physical properties, is gradually produced from phosphorus pentachloride when exposed to moist air. It is, however, better prepared by heating the pentachloride with certain acids or with compounds containing water chemically combined. The best substance to employ for this purpose is ordinary crystallized boric acid, which is then converted into boric anhydride:—

$$3PCl_5 + \underset{\text{Boric acid}}{2B(OH)_3} = 3POCl_3 + \underset{\text{Boric anhydride}}{B_2O_3} + 6HCl.$$

Phosphorus pentachloride and boric acid are mixed in the proportions shown in the equation—*i.e.* about five parts of the former with one part of the latter—the mixture placed in a retort, and then heated. Torrents of hydrochloric acid are given off, and phosphoric oxychloride distils over into the well-cooled receiver. The boric anhydride, which finally remains behind in the retort, may be dissolved up in warm water, allowed to crystallize, and again used for the same purpose.

Phosphoric oxychloride is a colourless liquid sinking in water, by which it is soon decomposed. It has a specific gravity of 1·7, boils at 110°, fumes when exposed to the air, and possesses a piercing odour. It is easily decomposed by water into hydrochloric and phosphoric acids.

Corresponding to phosphoric oxychloride is a sulphur compound, *phosphoric sulphochloride*: $PSCl_3$, which is also a colourless liquid,

of specific gravity 1·6 and boiling at 125°. It fumes in the air and is slowly decomposed by water into phosphoric acid, hydrochloric acid, and sulphuretted hydrogen. This compound is obtained by heating phosphorus pentachloride with certain metallic sulphides—*e.g.* antimonous sulphide :—

$$3PCl_5 + \underset{\substack{\text{Antimonous}\\ \text{sulphide}}}{Sb_2S_3} = 3PSCl_3 + \underset{\substack{\text{Antimonous}\\ \text{chloride}}}{2SbCl_3}.$$

BROMIDES OF PHOSPHORUS.

Phosphorus Tribromide (*Phosphorous Bromide*) : PBr_3.

This is a heavy colourless liquid, of specific gravity 2·9, boiling at 173°, and closely similar in its chemical properties to the corresponding trichloride. It is best obtained by dissolving a known weight of phosphorus in about eight times as much carbon disulphide, and then dropping in the requisite quantity of bromine—*i.e.* three atoms of bromine for every atom of phosphorus. As soon as the reaction has ceased and all bromine has disappeared the carbon disulphide is evaporated off on a water bath, and then the phosphorus tribromide distilled over.

Phosphorus Pentabromide (*Phosphoric Bromide*) : PBr_5.

The pentabromide is prepared in precisely the same way as the tribromide, except that five atoms of bromine for every atom of phosphorus are employed.

It is a yellow, crystalline solid, less stable than phosphorus pentachloride, decomposing even at 100° into phosphorus tribromide and bromine. When acted upon by water it behaves in a similar manner to the corresponding pentachloride.

Phosphoric Oxybromide : $POBr_3$, is a crystalline solid, melting at 45° and boiling at 195°. It is obtained, together with acetyl bromide and hydrobromic acid, by acting on phosphorus pentabromide with acetic acid :—

$$PBr_5 + \bar{A}OH = POBr_3 + \bar{A}Br + HBr.$$

IODIDES OF PHOSPHORUS.

We have already remarked that phosphorus penta-iodide is unknown ; only the tri- and di-iodides have been as yet prepared. Both are obtained in the same way—viz. adding the requisite quantity of iodine to a solution of phosphorus in carbon disulphide.

Phosphorus Tri-iodide : PI_3, is soluble in carbon disulphide, but separates out as red crystals when the liquid, after distilling off the disulphide, is placed in a freezing mixture. It melts at 55°, gives off iodine at its boiling temperature, and is easily decomposed by water into phosphorous and hydriodic acids.

Phosphorus Di-iodide : P_2I_4, can be obtained not only by the method indicated above, but also by the direct union of solid phosphorus and iodine. For this purpose a flask is filled with carbonic acid gas and the phosphorus and iodine introduced in the correct proportions. On contact they combine energetically with one another, forming a dark-coloured liquid, which, when the reaction has been completed by slight rise in temperature, solidifies to a crystalline mass on cooling. When this mass is dissolved in hot carbon disulphide, phosphorus di-iodide is deposited on cooling as bright orange coloured tablets or prisms. The di-iodide melts at 110° to a bright red liquid, and is decomposed by water into hydriodic acid, phosphorous acid, and amorphous phosphorus :—

$$3P_2I_4 + 12H_2O = 4HPO(OH)_2 + 12HI + 2P.$$

COMPOUNDS OF PHOSPHORUS WITH SULPHUR.

Phosphorus and sulphur unite in several proportions with one another. They have a strong attraction for one another, and their union is accompanied with so considerable an evolution of heat that if large quantities are employed disastrous explosions may be produced.

But if amorphous phosphorus is employed, large quantities of these compounds may be easily and safely prepared. Powdered

sulphur and amorphous phosphorus are mixed together, and the mixture heated in a closed Hessian crucible. The crucible is first gently heated, and then more strongly after the reaction has taken place. The two substances unite with one another at the moment when the amorphous phosphorus passes into the common form. A large quantity of heat is given off, but no explosion takes place. If sulphur is in excess phosphorus pentasulphide: P_2S_5, is produced, while with excess of phosphorus, tetraphosphoric trisulphide: P_4S_3, is formed.

Phosphorus Pentasulphide (*Phosphoric Sulphide*): P_2S_5, may also be prepared by heating yellow phosphorus with sulphur and carbon disulphide in sealed tubes at 210°. On cooling, the compound separates out in long yellow needles. It melts at 210°, boils without decomposition at about 519°, and is decomposed by water into phosphoric acid and sulphuretted hydrogen.

Tetraphosphoric Trisulphide: P_4S_3, is easily soluble in cold carbon disulphide, from which it crystallizes in long, yellow, rhombic prisms, which melt at 166° and are only slowly decomposed by water into phosphorous acid and sulphuretted hydrogen.

The solution of this substance in carbon disulphide, after heating with sulphur, yields yellow crystals of a compound possessing the formula P_2S_4.

ARSENIC.

Chemical Symbol: As.—*Atomic Weight*: 75.

Arsenic occurs in nature both native and in chemical combination with other elements. Native arsenic is sometimes found in the crystalline state, but it generally occurs in rough lumps, which easily break up into uneven laminæ. More common in nature are its compounds, of which the following are the most important: *Arsenical iron*, $FeAs_2$; *arsenical iron pyrites* or *mispickel*, FeSAs; *Kupfer-nickel*, NiAs; *smaltite* or *tin white cobalt* $(Co,Ni,Fe)As_2$; *realgar*, As_2S_2; *orpiment*, As_2S_3. Besides these, arsenic is also found in combination with oxygen as *white arsenic*: As_4O_6, and in

the form of arsenic acid in various minerals, such as *pharmacolite*, *cobalt-bloom*, *mimetesite*, &c. Finally, it is a very remarkable fact that arsenic, probably as arsenious acid, has been discovered in many mineral springs, in those of Em's, Kissingen, Pyrmont, Schwalbach for example. The quantity is, however, so extremely small that the physiological action of the mineral waters can scarcely be ascribed to its influence.

Arsenic (commonly called 'metallic' arsenic to distinguish it from 'white' arsenic, the oxide), when freshly broken, possesses a steel-grey colour, and strong metallic lustre. It is very brittle, and may therefore easily be reduced to powder. Its specific gravity is 5·7. When heated arsenic sublimes and condenses partly as an amorphous mass, and partly as rhombohedra; it may be melted under increased pressure. The specific gravity of its vapour at about 860° is 10·2, which corresponds to a molecular weight of about 300, or, in other words, its molecule in the gaseous state contains four atoms. In this abnormal property arsenic resembles, therefore, phosphorus and sulphur.

When exposed to moist air arsenic loses its metallic lustre, and becomes dull in consequence of surface oxidation. It is insoluble in water, but if the water contains air a small quantity of the arsenic is oxidized by the oxygen of the air to arsenious acid, which then dissolves in the water.

When heated in the air arsenic volatilizes and burns, forming white fumes of arsenious anhydride. At the same time an unpleasant garlic-like odour is noticed, which is perhaps peculiar to arsenic vapour, or is perhaps due to a lower oxide. Heated in oxygen, arsenic burns with a large evolution of light and heat, also producing arsenious anhydride. Finely powdered arsenic, when shaken into a jar of chlorine, catches fire and burns to arsenious chloride. Nitric acid oxidizes arsenic to arsenious or arsenic acid accordingly as the arsenic or nitric acid is in excess. In the same way concentrated sulphuric acid also oxidizes arsenic, and is itself reduced to a sulphurous anhydride. Hydrochloric acid scarcely acts upon it.

Native arsenic is never pure. It may be obtained pure by sublimation from arsenical iron pyrites, which breaks up when heated into ferrous sulphide and metallic arsenic.

Arsenic is chiefly used in the arts for hardening lead in the manufacture of shot

ARSENIURETTED HYDROGEN (**Arsine**).

Composition : AsH_3.

This substance, corresponding to ammonia in composition, is the best known compound of arsenic and hydrogen. In consequence of the weak affinities of the two elements for one another no compound can be prepared by their direct union.

Arseniuretted hydrogen is a colourless gas, with a repulsive odour resembling garlic, and only slightly soluble in water. It is condensed at $-40°$ to a colourless liquid, and burns when ignited in the air with a livid flame forming water and arsenious anhydride. The specific gravity of the gas is 2·7, corresponding to the molecular formula : AsH_3. Arseniuretted hydrogen is one of the most deadly poisons with which we are acquainted ; it is more poisonous than any other compound of arsenic. The chemist Gehlen lost his life by inhaling this gas, and fatal effects have also been produced in some other cases. Experiments with arseniuretted hydrogen must therefore be undertaken with great care, and the conditions under which the gas may be produced ought to be well known.

Arseniuretted hydrogen is produced in all cases when nascent hydrogen and arsenic are brought together, especially in acid liquids. In considerable quantities it may be obtained by acting on an alloy of zinc and arsenic (prepared by adding two parts of arsenic to three of melted zinc, and pouring the alloy into cold water) with dilute hydrochloric acid. The reaction is illustrated by the following equation :—

$$As_2Zn_3 \quad + \quad 3SO_2\begin{cases}OH\\OH\end{cases} \quad = \quad 3SO_2 \cdot O_2Zn \quad + \quad 2AsH_3.$$

Since commercial zinc nearly always contains small quantities of arsenic, the hydrogen which is prepared from zinc is nearly always contaminated with arseniuretted hydrogen. On the other hand, commercial hydrochloric and sulphuric acids also contain traces of arsenic as arsenious acid, and when such acids are used for the preparation of hydrogen, the nascent hydrogen reduces the arsenious acid to arseniuretted hydrogen :—

$$As_4O_6 \quad + \quad 12H_2 \quad = \quad 6H_2O \quad + \quad 4AsH_3.$$

On adding a few drops of a solution of arsenious acid to an appa ratus evolving hydrogen from zinc and sulphuric acid, a mixture of hydrogen with sufficient arseniuretted hydrogen to exhibit its most

important properties is obtained. It is extremely dangerous to prepare the nearly pure gas from the alloy of zinc and arsenic. The production of the gas from a solution of arsenious acid and nascent hydrogen is used to detect extremely minute quantities of arsenic.

The two constituents are so loosely combined in arseniuretted hydrogen, that the compound is decomposed at a low red-heat into arsenic and hydrogen. When led in a slow stream through a red-hot glass tube, the inner walls of the tube just beyond the heated portion become coated with a lustrous, dark brown mirror of reduced arsenic. The mirror of arsenic may be readily observed when very minute quantities of the gas mixed with much hydrogen are passed through the hot tube. The same decomposition takes place when a jet of arseniuretted hydrogen is inflamed in the air. By the high temperature of the flame the unburnt gas in its interior is decomposed into hydrogen and arsenic, and it is this finely divided arsenic which imparts to the flame its pale livid colour. That free arsenic is really present in the interior of the flame may be readily proved by pressing a piece of cold white porcelain, such as a porcelain dish, down upon the flame. The cold porcelain becomes coated with a round stain of brown arsenic at the spot where the flame has touched it. The same phenomenon is produced, though less intense, if the gas is mixed with a large quantity of hydrogen.

It is well known that wall-papers printed with colours (especially bright greens) containing arsenic exercise an injurious influence on persons living or sleeping in rooms so papered. The papers are fastened to the walls with starch paste, which easily ferments and sets free nascent hydrogen. And since the whole thickness of the paper is saturated with the paste, this nascent hydrogen comes directly into contact with the arsenic compounds, and reduces them to arseniuretted hydrogen, which then poisons the air of the rooms. The quantity of the gas produced is of course very minute, but often sufficient to produce very injurious effects, and sometimes a faint unpleasant smell may also be observed. The sale of such papers ought therefore to be forbidden by law.

That the arsenic and hydrogen are only feebly united in arseniuretted hydrogen is also shown by its general chemical behaviour. Chlorine decomposes the gas at once into arsenious chloride and hydrochloric acid, producing a large quantity of light and heat. This is easily shown by leading the gas into a cylinder containing chlorine.

Arseniuretted hydrogen led into a solution of silver nitrate produces a black precipitate of metallic silver, while both the hydrogen and arsenic are oxidized :—

$$4AsH_3 + 24NO_2{\cdot}OAg + 6H_2O = 24NO_2{\cdot}OH + 24Ag + As_4O_6.$$

With copper sulphate it precipitates copper arsenide.

SOLID ARSENIURETTED HYDROGEN $(AsH)_n$.

A brown velvet-like substance produced by the action of the silent electric discharge upon arsine or of water upon potassium or sodium arsenide.

OXIDES AND OXY-ACIDS OF ARSENIC.

Two of these compounds are known—arsenious anhydride and arsenic anhydride—both of which are soluble in water and then produce the corresponding acids. The former is a weak acid only slightly soluble in water, while the latter is easily soluble, and is a strong acid. The two oxides possess an analogous composition to that of phosphorous and phosphoric anhydrides, and arsenic acid, like common phosphoric acid, is tribasic.

Just as when sulphur is burnt, sulphurous anhydride is produced and not sulphuric anhydride, so too the combustion of arsenic always produces arsenious anhydride and not arsenic anhydride. We can, however, easily oxidize arsenic, or the lower oxide, to arsenic acid by nitric acid, in the same manner as we obtain sulphuric acid from sulphur or its lower oxide.

ARSENIOUS ANHYDRIDE (**White Arsenic**)

Composition : As_4O_6.

This oxide of arsenic is found in small quantities in nature as the mineral ***arsenic-bloom***, and is produced on a large scale by roasting various minerals containing arsenic in a free supply of air. The volatile products so produced, which consist chiefly of sulphurous and arsenious anhydrides, are led through long passages and chambers, where the arsenious anhydride is deposited as a white crystalline powder. It is brought into trade partly in this form, and partly as a vitreous, amorphous solid.

Arsenious anhydride is odourless, both in the solid and gaseous states. It possesses a faint sweetish taste. Three modifications of

this substance are known—one amorphous and vitreous, the two others crystalline. The former is prepared by subliming the white crystalline powder, already described, in upright iron retorts at as high a temperature as possible, when the vitreous form is deposited in crusts on the neck of the retort.

Vitreous arsenious anhydride is a transparent, lustrous, amorphous solid, breaking with a conchoidal fracture. It has a specific gravity of 3·72, and gradually changes from the exterior to the interior into octahedral crystals, and assumes the appearance of white porcelain. Pieces of vitreous arsenious anhydride which have been prepared for some time are found, when broken, to contain only a small nucleus of the transparent kind, all the rest having changed into the crystalline variety.

This crystalline modification has a somewhat smaller specific gravity (3·62), and is less soluble in water than the vitreous kind. One part of the former requires 355 parts of water for its solution at the ordinary temperature, while one part of the latter dissolves in 108 parts of water; in boiling water more of each variety is dissolved. A hot saturated aqueous solution, on cooling, deposits arsenious anhydride in regular octahedra. The aqueous solution faintly reddens litmus paper. It is remarkable that, although arsenious anhydride is much less soluble in water than arseni anhydride, it is still far more poisonous than this latter compound. Hydrochloric acid dissolves much larger quantities of arsenio anhydride than water. Nitric acid oxidizes it to arsenic acid, an is itself reduced to nitrous anhydride and nitric peroxide (p. 194

Arsenious anhydride sublimes when heated without meltin and is deposited, if rapidly cooled, in brilliant transparent oct hedra, but, if slowly cooled, in crystals belonging to the rhomb system, and of specific gravity 4·3.

The vapour density of arsenious anhydride, even at a wh heat, is 13·8, which corresponds to a molecule consisting of fo atoms of arsenic united with six atoms of oxygen. It is, howev probable that if the vapour density could be determined at a higl temperature it would be found to be only one-half as great, in other words, that the molecules of arsenious anhydride wh are represented by the formula As_4O_6 would break up into molecu of half the weight, just as those of sulphur vapour, which cont six atoms at a temperature of about 100° above its boiling po break up at a higher temperature into molecules only one-thir

Arsenious Acid: $As(OH)_3$, is probably contained in an aqueous solution of arsenious anhydride, but has not yet been prepared in the free state. It is a tribasic acid. With the alkalies it forms soluble salts; its other compounds are insoluble or difficultly soluble in water, but are easily dissolved by acids, even by excess of arsenious acid itself. Its compounds are in general but little known; many are unstable because of the weak affinities of the acid. The ammonium compound, obtained by saturating an aqueous solution of the acid with ammonia, loses all its ammonia on evaporation and finally leaves only arsenious anhydride behind. If to an aqueous solution of arsenious acid silver nitrate is added, no precipitate of silver arsenite is formed; because the nitric acid, which is set free on the production of this compound, keeps it in solution. But on the addition of one drop of ammonia, which neutralizes the nitric acid, a bright yellow precipitate is obtained, very similar to silver phosphate in appearance. It is also soluble in ammonia, and care must therefore be taken not to add too much of this reagent. Arsenious acid or its salts are at once distinguished from phosphoric acid or its salts by the production of a yellow precipitate of arsenious sulphide, when sulphuretted hydrogen is led through their slightly acid solution.

The double compound of copper arsenite and copper acetate (Schweinfurt green), as well as an acid copper arsenite (Scheele's green), are brilliant green pigments. Both are extremely poisonous, and are therefore but little employed; they should never be used for paper-hangings, textile fabrics, toys, and other similar articles.

No substance has been for so long and so often the cause of death by poisoning both accidentally and intentionally as arsenious anhydride. Its external appearance, particularly its similarity to common flour, its slight taste, and lack of odour combine to render it particularly dangerous. Doses of 0·12 gramme (2 grains), or even less, often produce fatal effects. Chemists have, therefore, endeavoured to discover, firstly, some substance which, when taken internally, shall counteract the action of the poison—*i.e.* act as an *antidote*; secondly, some method by means of which arsenic may be readily and certainly discovered in the bodies of persons who are supposed to have been poisoned by it. Both these objects have now been attained.

Notwithstanding its poisonous properties, it is a remarkable fact that some animals—*e.g.* horses—can take large doses of arsenic

without any ill effects. On the contrary, it improves their general appearance and makes their coats more glossy. Doses, even as large as 15 grammes, have also been given to sheep without apparent injury. In the same way man himself may become accustomed to the use of arsenic. The so-called *arsenic eaters* of the Tyrol, who commence with small doses, at last take as much as $\frac{1}{4}$ gramme daily and even more. They thus become stouter, look healthier, and can ascend mountains more easily. Symptoms of arsenic poisoning only make their appearance when the use of the poison is discontinued.

For more than 2,000 years it was vainly endeavoured to discover some substance which should act as an antidote to arsenic. In 1834, however, Bunsen discovered such a substance in ferric hydrate, which, when taken soon enough, nearly always entirely counteracts the injurious effects of the poison. This discovery was not the result of accident, but was due to simple deductions from chemical facts. Bunsen found during his investigations on arsenious acid that ferric arsenite is quite insoluble in water; it was also known that substances insoluble in water and the gastric juice do not exercise any poisonous action on the animal body. From this he argued that if ferric hydrate in a suitable form were introduced into the stomach of persons who had taken arsenious acid, this insoluble and innocuous ferric arsenite would be formed and afterwards expelled from the body.

His expectations were realised in a remarkable degree, and since then many valuable lives have been saved by the action of this antidote. It is only the freshly precipitated hydrate which possesses this action. If the hydrate is kept for long, even when mixed with water, it undergoes a molecular change and becomes much weaker in its action. One of the best methods of administering the antidote is as follows. A solution of ferric sulphate, prepared by oxidizing ferrous sulphate, is mixed with calcined magnesia (magnesium oxide). The substances then produced are the red-brown insoluble ferric hydrate and soluble magnesium sulphate (Epsom salt), which remains in solution :—

$$(SO_2)_3O_6Fe_2 + 3MgO + 3H_2O$$
$$= Fe_2(OH)_6 + 3SO_2 \cdot O_2Mg.$$

The ferric hydrate combines with the arsenious acid, while the accompanying magnesium sulphate acts as a powerful purgative and rapidly removes the arsenic from the system.

DETECTION OF ARSENIC IN CASES OF SUSPECTED POISONING.

In cases of suspected poisoning by arsenic, it is first necessary to make a mechanical examination of the vomit or of the contents of the stomach to discover, if possible, white grains of unabsorbed arsenious anhydride. If such are found they are carefully collected and subjected to a special examination.

One or two of these grains are placed at the end of a closed glass tube drawn out to a fine point, above which a small splinter of freshly glowed wood-charcoal is allowed to fall, as shown in

Fig. 48.

fig. 48. The splinter of charcoal is now gently heated in a gas flame until faintly glowing, and the tube is then slightly inclined so as to bring its extreme end into the flame. If the substance is arsenious anhydride it is converted into vapour, which on passing over the red-hot charcoal is reduced, its oxygen uniting with the charcoal, the reduced arsenic being deposited in the cooler parts of the tube above the charcoal as a lustrous black ring (fig. 49).

Fig. 49.

To be sure that this metallic mirror is really arsenic, the end of the tube is cut off when cold, the piece of charcoal allowed to drop out, and the mirror gently heated. The arsenic is then again converted into vapour, recombines with the oxygen contained in the warm air passing through the tube, and is deposited in the form of arsenious anhydride as a white crystalline coating in the upper and cooler parts of the tube. At the same time the garlic-like odour, produced when arsenic is volatilized, is noticed at the upper end of the tube.

The white deposit of arsenious anhydride must dissolve in one drop of hydrochloric acid, and the solution, with the tube itself, when dropped into a test-tube containing sulphuretted hydrogen water, must give a bright yellow precipitate of arsenious sulphide.

Whether white grains of free arsenious anhydride have been found or not, it is usually necessary to look for the arsenic, which may be intimately mixed or chemically combined with the organic matter of the stomach and other organs. For this purpose it is first necessary to destroy the organic matter in the following manner.

The organs are cut into small pieces, placed in a porcelain basin, and heated on the *water-bath* with chemically pure hydrochloric acid, while small quantities of potassium chlorate are added from time to time. The chlorine which is liberated from the mixture of hydrochloric acid and potassium chlorate destroys the organic substances and oxidizes the arsenic to arsenic acid. The mixture must not be heated over the naked flame, or at least not boiled, for if this were done arsenic chloride would pass off with acid vapours and so be lost. As soon as the potassium chlorate has been completely destroyed, which may be easily recognized by the liquid no longer smelling of chlorine—the hydrochloric acid being of course in excess—the liquid is filtered and the residue well washed with hot water. All the arsenic, in the form of arsenic acid, is now contained in the solution, together with small quantities of organic compounds. From the clear liquid the arsenic is thrown down as arsenious sulphide by a long-continued stream of well-washed sulphuretted hydrogen. Arsenic acid, unlike arsenious acid, is not precipitated *at once* by sulphuretted hydrogen, but only after some time. The first action of the gas is to reduce the arsenic acid to arsenious acid, free sulphur being at the same time precipitated. The yellow precipitate consists therefore of a mixture of sulphur and arsenious sulphide.

As soon as the liquid smells strongly of sulphuretted hydrogen and has been allowed to stand for about twelve hours in a warm place, the precipitate—usually dark-coloured from organic impurities—is collected on a small filter and well washed. The moist filter paper with the precipitate is then spread out inside a small porcelain dish, carefully dried, and moistened with pure concentrated sulphuric acid. On gently warming the dish, the paper is completely charred and destroyed, as well as the traces of organic substances mixed with the precipitate ; a few drops of pure nitric acid or a crystal of nitre then completely oxidizes the arsenious sulphide again to arsenic acid. The filtered solution now contains the whole of the arsenic originally present in combination

with oxygen as arsenic acid, and it now remains to prove in a certain manner the presence or absence of this substance.

This is done by means of *Marsh's apparatus*, in which arsenic acid or arsenious acid is reduced to arseniuretted hydrogen, a gas easily yielding free arsenic when decomposed by heating.

Marsh's apparatus, so called after its discoverer, consists of a two-necked Woulffe's bottle (fig. 50) furnished with a funnel-tube and a delivery-tube, both fitted gas-tight through good, sound corks. The short, bent delivery-tube is attached by a sound cork to a piece of difficultly fusible glass (called combustion-tube) which has been previously narrowed in several places, and of which the end is bent upwards at right angles, and terminates in a small jet. The front part of this tube is packed loosely with cotton-wool or

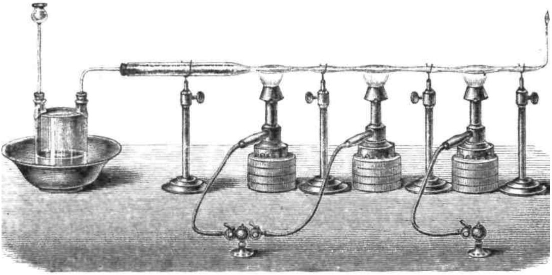


Fig. 50.

glass-wool, to retain any liquid which might be mechanically carried over from the Woulffe's bottle by the gas. The tube is supported in several places so that it may not bend when afterwards heated.

After a quantity of granulated zinc, free from arsenic, has been introduced into the Woulffe's bottle and the apparatus arranged as described, a cold mixture of pure sulphuric acid with about eight times its volume of water, prepared beforehand, is poured into the flask through the funnel tube. The hydrogen, which is at first evolved slowly, but afterwards more rapidly, is allowed to pass through the apparatus until all the air has been expelled. The gas is then ignited at the jet, and the tube strongly heated in several places by separate powerful burners.

This preliminary experiment is to decide whether the substances employed—the zinc and the sulphuric acid—are absolutely free from arsenic. If either contains even traces of arsenic, this substance is always converted by the nascent hydrogen into arseniuretted hydrogen. This latter gas, even when mixed with a large excess of hydrogen, is decomposed when heated to redness in the tube into arsenic and hydrogen, and the former is deposited as a brilliant black ring or mirror on the cooler parts of the tube just beyond the portions heated.

Should the stream of gas be rapid, small quantities of arseniuretted hydrogen may remain undecomposed, but are at once detected by pressing a cold white porcelain dish on the jet of burning gas. If arsenic is present, that part of the porcelain dish in contact with the flame becomes covered with a brown stain of arsenic.

If after ten minutes of continued heating no trace of a mirror is formed in the tube, and the porcelain dish when pressed down in the flame remains perfectly white, it is absolutely certain that both the zinc and the sulphuric acid contain no arsenic.

The dilute sulphuric acid solution which is to be tested for arsenic is now gradually poured into the Woulffe's bottle, while the tube is continuously heated in several places and the jet at the end kept ignited. The rate at which the gas is evolved is to be regulated by pouring in acid or by placing the bottle in cold water: it was for this purpose previously placed in an empty basin. The rapidity of the stream of gas is known by the height of the flame at the jet; it should be regulated until the flame is about three centimetres (one inch) high. If arsenic is present, as many of the mirrors as possible, both in the tube and on porcelain dishes, should be prepared in order to prove by further experiments that they really consist of arsenic. And when cold the glass tube is afterwards cut up into as many pieces as it contains mirrors.

Even with all the precautions which have just been enumerated, there is still a possibility of error. The oxides of antimony, like those of arsenic, are also reduced by nascent hydrogen, producing gaseous antimoniuretted hydrogen, which, like the arsenic compound, is decomposed at a red heat into its constituents—antimony and hydrogen. If, therefore, the suspected liquid contains no arsenic but antimony, mirrors of antimony are obtained in the Marsh's apparatus which can scarcely be distinguished by the naked eye from those of arsenic.

And when it is remembered that in cases of suspected poisoning an emetic is nearly always given to remove the poison as quickly as possible from the stomach, and that one of the most powerfully acting of these substances is tartar emetic (a compound of tartaric acid, potassium, and antimony), it will be at once seen that on treating the contents of the stomach by the above process, mirrors of antimony may be obtained indistinguishable from those of arsenic without further experiments.

To be quite sure that the mirrors (if obtained) are arsenic and not antimony, the following experiments may be tried :—

1. One of the pieces of glass tube containing a mirror is immersed in a freshly prepared solution of sodium hypochlorite. If the mirror is of arsenic it disappears almost immediately, while if of antimony it remains unchanged in the liquid for more than twenty-four hours.

2. A second piece of tubing containing a mirror is inclined at an angle and gently heated. Both antimony and arsenic are thus oxidized, the former to antimony tetroxide, the latter to arsenious anhydride, which are deposited on the upper and cooler parts of the tube. Both these white deposits dissolve readily in a drop of warm hydrochloric acid, but on dipping them into sulphuretted hydrogen water, the antimony gives an orange-coloured precipitate of antimonous sulphide, while the corresponding sulphide of arsenic obtained in the same way is bright yellow.

3. The mirrors obtained by depressing a piece of cold porcelain on a jet of the burning gas are treated with yellow ammonium sulphide (containing dissolved sulphur). Both arsenic and antimony dissolve (the latter more quickly), and so produce compounds of ammonium sulphide with arsenic and antimony sulphides respectively. If, then, both are evaporated to dryness, yellow arsenic sulphide is produced from the former and orange antimony sulphide from the latter. The orange antimony sulphide is at once dissolved by a few drops of warm hydrochloric acid, but the yellow arsenic sulphide remains unchanged.

Such investigations to discover the presence or absence of arsenic are not of themselves difficult. But they require great care and experience on the part of the chemist ; he must be absolutely certain (i.) that small quantities of arsenic have not escaped him, (ii.) that arsenic was not contained in the reagents or vessels employed and so have been found when not really present in the original substance ; and, finally, that antimony has not been mis-

taken for arsenic. In criminal cases, where his decision may be a question of life or death, the investigations should be conducted with even greater care, and only chemists of long experience should be employed.

Among the minor precautions which must be remembered and attended to in such investigations are the following.

Pure diluted sulphuric acid and pure zinc evolve pure hydrogen without a trace of sulphuretted hydrogen, even when the liquid becomes heated. But if concentrated sulphuric acid is added by a funnel tube to a mixture of zinc and water, the hydrogen is found to be mixed with sulphuretted hydrogen, the latter gas being produced by the action of the nascent hydrogen upon the sulphurous anhydride formed under these circumstances (p. 160). If arsenious acid is present in this liquid it is at once converted into arsenious sulphide, upon which nascent hydrogen has no action.

If, therefore, concentrated acid is poured into the Marsh's apparatus—*e.g.* to accelerate the evolution of gas—and the solution to be tested for arsenic then added, even if the latter substance were present, no mirror or only a minute one of arsenic would be produced, because the arsenic would remain behind in the flask as arsenious sulphide.

For the same reason granulated zinc which has lain in the laboratory for some time and of which the surface has become covered with a thin coating should first be digested with dilute sulphuric acid and washed. This coating is not always simply zinc oxide, but may contain zinc sulphide, which would produce sulphuretted hydrogen in the Marsh's apparatus and lead to the formation of arsenious sulphide.

Since sulphurous acid, in acid solutions, is reduced by nascent hydrogen to sulphuretted hydrogen, care must be taken that the liquid before introduction into the Marsh's apparatus is perfectly free from this substance. A mere trace of sulphurous acid would form arsenious sulphide, and so be a source of error.

If the liquid to be tested contains organic matter suspended or dissolved when introduced into the Marsh's apparatus, it might be volatilized or particles of it might be carried over mechanically by the stream of gas, and become carbonized at the heated portions of the tube. A dark lustrous deposit of carbon might thus be produced similar to the arsenic mirror. It is, for this reason, absolutely necessary to remove the whole of the organic matter by treating the original substance with hydrochloric acid and

potassium chlorate, and by acting on the sulphuretted hydrogen precipitate with concentrated sulphuric acid.

In some cases the dried substance might be at once charred with concentrated sulphuric acid to destroy organic matter, without first acting upon it with hydrochloric acid and potassium chlorate. This, however, is only permissible when the substance is free from common salt or other metallic chlorides. In such cases hydrochloric acid is formed, which unites with the arsenious anhydride to form volatile arsenious chloride, and this passes away with the vapours, and is lost. And as the organs of the human body nearly all contain common salt, this charring with sulphuric acid is inadmissible.

It is of course of the utmost importance to test the various substances employed in the investigation for arsenic. The sulphuric acid, zinc, hydrochloric acid, potassium chlorate, the nitric acid or nitre and even the filter papers and water must all be previously brought into the Marsh's apparatus for this purpose. It is also better in all important (criminal) cases to employ exclusively new vessels and apparatus which have never previously been used for chemical purposes.

A further complication arises when the substance to be tested for arsenic contains antimony. Mirrors are then produced in the Marsh's apparatus, but no definite result can be obtained, especially when only relatively small quantities of arsenic are present. If the mirror does not apparently dissolve when dipped into a solution of sodium hypochlorite, it does not follow that arsenic is absent.

We owe to Fresenius a very simple and exact method of detecting arsenic in presence of much larger quantities of antimony. This method depends upon the fact that arsenic is easily volatilized at a low red heat, but antimony only at a much higher temperature, and that the sulphides of both metals are easily reduced when heated with potassium cyanide, which is then converted into potassium sulphocyanate. The practical details are as follows.

The substance to be tested for arsenic is treated as described above, except that finally the antimony and arsenic are precipitated as sulphides by a continued stream of sulphuretted hydrogen, and the sulphides washed and dried. The dried sulphides are then rapidly mixed in a warm mortar with about four times as much of a mixture of 1 part of potassium cyanide and 3 parts of dry sodium carbonate. This mixture is introduced quickly (to avoid abstraction

of moisture from the air) into a short piece of glass tubing open at both ends and this slipped into a piece of combustion tube drawn out at one end. A carbonic acid apparatus is connected with this tube as shown in fig. 51.

As soon as all the air is expelled the stream of carbonic acid is so regulated that it only passes quite slowly. Various positions of the narrow portion are now heated to low redness, and then the mixture of the two sulphides, with sodium carbonate and potassium cyanide.

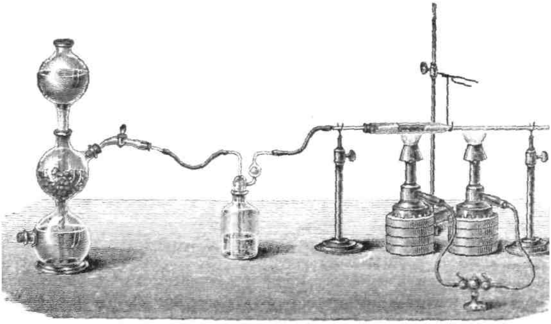


Fig. 51.

Both sulphides are thus reduced to arsenic and antimony respectively. The latter remains with the mixture, while the former is volatilized and deposited beyond the heated portions of the narrow tube as ordinary arsenic mirrors which exhibit all the properties of this element. At the same time a *small* quantity of arsenic is carried over with the carbonic acid, imparting to the gas issuing from the end of the tube the well-known intense garlic odour of arsenic.[1]

ARSENIC ANHYDRIDE : As_2O_5, and ARSENIC ACID : $AsO \cdot (OH)_3$.

On the combustion of arsenic in oxygen, the lower oxide, arsenious anhydride, and not the higher, arsenic anhydride, is always produced, because the latter compound is decomposed at the tem-

perature of combustion of arsenic into arsenious anhydride and oxygen. We have already seen (p. 156) that for the same reason sulphur always burns to sulphurous anhydride and not to sulphuric anhydride. The oxidation can, however, be readily effected in what is called the wet way by nitric acid, which easily gives up oxygen to many substances.

When arsenious anhydride is heated with nitric acid large quantities of red fumes consisting of nitric peroxide and nitrous anhydride are evolved; and if the strongly acid liquid is evaporated down to a syrup in order to expel the excess of nitric acid, crystals of arsenic acid united with water: $2AsO(OH)_3 + H_2O$, separate out on cooling in rhombic plates. These crystals are very deliquescent; they melt at 100° and lose their water of crystallization, leaving pure arsenic acid.

Arsenic acid so obtained is a strong acid, and, like ordinary phosphoric acid, is tribasic. It also loses water when heated to about 180°, forming tetrabasic *pyroarsenic acid*: $O \begin{cases} AsO(OH)_2 \\ AsO(OH)_2 \end{cases}$ At a higher temperature, about 200°, a further quantity of water is given off and the acid becomes monobasic *metarsenic acid*: $AsO_2 \cdot OH$, which, finally, at a low red heat is converted into arsenic anhydride: As_2O_5, thus:—

$$2AsO_2 \cdot OH \quad - \quad H_2O \quad = \quad As_2O_5 \quad = \quad O \begin{cases} AsO_2 \\ AsO_2 \end{cases}$$

The anhydride is a white amorphous substance, only difficultly soluble in water, but which is gradually converted into ordinary tribasic arsenic acid when allowed to stand for some time in contact with water. At temperatures above a red heat arsenic anhydride breaks up into arsenious anhydride and oxygen.

Even at ordinary temperatures arsenic acid in solution readily gives up oxygen to many substances, as, for example, sulphuretted hydrogen, sulphurous anhydride, stannous chloride, &c., and is reduced to arsenious acid. Nascent hydrogen evolved in acid liquids reduces arsenic acid, as well as arsenious acid, to arseniuretted hydrogen. In consequence of the readiness with which arsenic acid parts with oxygen, it is largely employed in the arts—principally to oxidize aniline, and to convert it into the brilliant aniline colour known as magenta or fuchsine.

Common or tribasic arsenic acid yields, like common phosphoric acid, three series of salts—the normal, monacid, and diacid salts. The two former are mostly insoluble, or difficultly

soluble, in water. Normal silver arsenate: $AsO(OAg)_3$, is thrown down as a chocolate-coloured precipitate on mixing solutions of the sodium salt and silver nitrate. It is easily soluble in nitric acid, and is at once distinguished from yellow silver arsenite by its colour. The monacid sodium arsenate corresponding to common sodium phosphate has the composition:—

$$AsO\begin{cases}(ONa)_2\\OH\end{cases} + 12H_2O,$$

and, like the phosphate, is obtained in fine clear crystals when its solution is slowly evaporated.

Arsenic acid, like phosphoric acid, also produces a yellow crystalline precipitate with a nitric acid solution of ammonium molybdate. And the compound of arsenic acid corresponding to ammonium-magnesium phosphate (p. 218), of the composition: $AsO\begin{cases}O_2Mg\\ONH_4\end{cases}$ is, like the phosphate, insoluble in water containing ammonia, and is therefore used for the quantitative determination of arsenic.

Arsenic acid, like arsenious acid, is precipitated as a yellow sulphide by sulphuretted hydrogen. This precipitation is not, however, *produced at once, as is the case with arsenious acid*, but only after some time, and then consists not of arsenic pentasulphide but of a mixture of the trisulphide and sulphur. By warming the solution, which assists the reduction of the arsenic acid to arsenious acid, the precipitation may be accelerated. Arsenic acid is poisonous, but, notwithstanding its much greater solubility in water, is far less so than arsenious acid.

COMPOUNDS OF ARSENIC WITH THE HALOGENS.

Arsenic, like phosphorus, combines directly with the halogens, but of these compounds only those are well known which contain triad arsenic. *Compounds containing one atom of arsenic united* with five atoms of chlorine or bromine have not yet been prepared. Iodides having the respective empirical formulæ, AsI_2 and AsI_5, have been described, but they have not been gasified.

Arsenious Chloride: $AsCl_3$, is a colourless, volatile, oily liquid, boiling at 130°, and with a specific gravity of 2·2. It is easily decomposed by water into hydrochloric and arsenious acids, and is therefore very poisonous. Its vapour density is 6·3, corresponding to the molecular weight represented by the formula: $AsCl_3$.

Arsenious chloride is produced by acting upon arsenic with dry chlorine, or better, by heating an intimate and dry mixture of 4 parts arsenious anhydride and 7 parts common salt with an excess of concentrated sulphuric acid in a retort provided with a receiver:—

$$As_4O_6 \ + \ 12NaCl \ + \ 12SO_2(OH)_2 \ = \ 4AsCl_3 \ + \ 12SO_2\begin{cases}OH\\ONa\end{cases} \ + \ 6H_2O.$$

The arsenious chloride then distils over, and acid sodium sulphate remains behind. The water, which is produced at the same time, is retained by the excess of sulphuric acid.

A simpler and better method of preparation consists in heating a mixture of powdered arsenic (1 part) with dry mercuric chloride (10½ parts) in a retort. The mercuric chloride then parts with one half of its chlorine, and is converted into mercurous chloride:—

$$2As \ + \ 6HgCl_2 \ = \ 2AsCl_3 \ + \ 3Hg_2Cl_2.$$

The chloride is purified by redistillation; it often possesses a violet colour.

Arsenious Bromide: $AsBr_3$, is also produced by the direct union of its elements, best by dissolving the dry bromine in perfectly dry carbon disulphide and then adding small quantities of powdered arsenic. By slow evaporation of the clear liquid poured off from the excess of arsenic in a current of dry air, arsenious bromide crystallizes out. It deliquesces when exposed to the air, and is easily decomposed by water, like the chloride, into hydrobromic and arsenious acids.

Arsenious Iodide: AsI_3, is prepared in a similar manner to that employed for the bromide, and crystallizes on evaporation of the solvent as brilliant red tablets. This compound is soluble in alcohol, and may be crystallized from its solution in this liquid. It is dissolved unchanged by cold water, but if the solution is

warmed decomposition ensues with formation of hydriodic and arsenious acids. Arsenious iodide is employed in medicine as a remedy for cancer.

Arsenious Fluoride: AsF_3, is produced as a colourless liquid by distilling equal parts of finely powdered fluor-spar and arsenious anhydride, with five parts concentrated sulphuric acid. It boils at 60° and fumes strongly in the air. Water first dissolves it, but decomposition into hydrofluoric and arsenious acids soon occurs.

COMPOUNDS OF ARSENIC WITH SULPHUR.

We are acquainted with three compounds of arsenic and sulphur—viz., a disulphide: As_2S_2; a trisulphide: As_2S_3; and a pentasulphide: As_2S_5; of which the two former occur in nature.

Arsenic Disulphide: As_2S_2. This compound is found in nature as fine red rhombic prisms as the mineral *realgar*. It may also be prepared from its constituents by heating a mixture of arsenic and sulphur in the proper proportions, or by heating a mixture of arsenious anhydride and sufficient sulphur, sulphurous anhydride being then evolved. It is insoluble in water, and is first decomposed and then dissolved by alkaline sulphides.

The substance which occurs in trade as a red vitreous mass under the name of *realgar*, *ruby-sulphur*, *red arsenic glass*, and which is used to some extent as a pigment, is not pure arsenic disulphide. It is prepared by distilling a mixture of arsenical pyrites (FeAsS) with common pyrites (FeS_2), and contains arsenic trisulphide, arsenious anhydride, or even free arsenic. This crude disulphide is employed for the manufacture of the so called Bengal fire. A mixture of 24 parts nitre, 7 parts sulphur, and 2 parts ruby-sulphur burns with a penetrating white light when ignited.

The corresponding oxide, of the composition: AsO or As_2O_2, has not yet been prepared.

Arsenic Trisulphide (Arsenious Sulphide): As_2S_3, occurs in nature as yellow rhombic prisms and is then called *orpiment*. Artificially it is prepared by heating together arsenic and sulphur in the proper proportions, or by passing a stream of sul-

phuretted hydrogen though an aqueous solution of arsenious acid, in the presence of hydrochloric acid. In the latter case the trisulphide is obtained on drying as a pale yellow, amorphous powder.

Arsenic trisulphide melts when heated to form a red liquid, which solidifies to a red semi-transparent glass. It is more transparent and gives a lighter coloured powder than the disulphide. Water and hydrochloric acid do not dissolve it, nitric acid oxidizes it to arsenic acid and sulphuric acid; it is also converted into arsenic acid by concentrated sulphuric acid, sulphurous anhydride being then set free. When mixed with potassium cyanide and heated in a glass tube it is reduced to arsenic, which sublimes, while the sulphur unites with the potassium cyanide forming potassium sulphocyanate, thus:—

$$3KCN + As_2S_3 = 2As + 3KCNS.$$

Arsenic trisulphide unites with basic sulphides to form sulpho-salts. The majority of these compounds are insoluble in water, but those containing the alkaline sulphides are soluble. It is at once dissolved by a cold solution of an alkaline sulphide, from which solution hydrochloric acid again precipitates the whole of the arsenic trisulphide. The potassium salt has the composition $AsS \cdot SK$, and its decomposition by dilute acids is shown in the following equation:—

$$2AsS \cdot SK + 2HCl = 2KCl + As_2S_3 + H_2S.$$

On mixing a solution of potassium sulpharsenite with solutions of silver, copper, or lead nitrate, a precipitate, usually coloured, of the corresponding silver, copper, or lead compound is produced, thus:—

$$AsS \cdot SK + NO_2 \cdot OAg = NO_2 \cdot OK + AsS \cdot SAg.$$

Caustic alkalies and even the alkaline carbonates also dissolve arsenic trisulphide, producing a mixture of an arsenite with a sulpharsenite. With caustic potash, for example, the reaction is as follows:—

$$2As_2S_3 + 4KOH = AsO \cdot OK + 3AsS \cdot SK + 2H_2O.$$

Arsenic Pentasulphide (Arsenic Sulphide): As_2S_5, is a yellow powder closely resembling the trisulphide in external properties, but which does not occur in nature. It might be supposed that sulphuretted hydrogen when led into a solution of arsenic acid would give a precipitate of arsenic pentasulphide, but this is not confirmed by experiment. The gas may be led into the acid liquid for a considerable time without producing any precipitate or even turbidity. Only after some time a yellow precipitate is gradually produced, which is not the pentasulphide, but a mixture of the trisulphide with free sulphur. That this is really the case may be proved by digesting the dried precipitate with carbon disulphide, which dissolves out the free sulphur, while yellow arsenic trisulphide remains behind.

Arsenic pentasulphide is best prepared by saturating a solution of potassium arsenate with sulphuretted hydrogen, and then decomposing the potassium sulpharsenate, so obtained, with dilute hydrochloric acid. The following equations represent the process:—

$$\text{(i.)}\quad \underset{\text{Potassium arsenate}}{AsO(OK)_3} + 4H_2S = \underset{\text{Potassium sulpharsenate}}{AsS(SK)_3} + 4H_2O.$$

$$\text{(ii.)}\quad 2AsS(SK)_3 + 6HCl = As_2S_5 + 6KCl + 3H_2S.$$

Arsenic pentasulphide combines with other sulphides and forms the sulpharsenates, corresponding to the above potassium compound.

ANTIMONY.

Chemical Symbol: Sb.—*Atomic Weight*: 120·2.

Antimony very seldom occurs free in nature, but is usually found combined with sulphur. Its commonest form is the trisulphide (Sb_2S_3)—the mineral called *grey antimony ore* or *antimonite*. This trisulphide also occurs in nature in combination with other sulphides as a sulpho-acid of which the minerals *chalcostibite* (Cu_2S,Sb_2S_3) and *dark red silver ore* or *pyrargyrite* ($3Ag_2S,Sb_2S_3$) are the commonest. In combination with nickel it is found as *breithauptite* (NiSb), and with silver as *dyscrasite* (Ag_4Sb).

In its physical properties antimony so closely resembles the metals, especially bismuth, that it is sometimes included in this group of elements. Its chemical properties and the compounds

which it forms show, however, that it is much more closely allied to the nitrogen group of the non-metals. It is a lustrous crystalline solid of a bluish-white colour, with a specific gravity of 6·7 ; melts at about 440°, and crystallizes on cooling in rhombohedra. When slowly cooled its fracture shows large crystalline laminæ, but when quickly cooled the fracture is granular. It is volatilized at a bright red heat, and may be distilled at a white heat in a stream of hydrogen gas.

The antimony of commerce is obtained almost exclusively from the trisulphide—grey antimony ore. The ore melts at a low temperature and can thus be easily separated from earthy impurities accompanying it. The purified ore which forms a dark grey, lustrous, and crystalline mass, is then heated to redness in a crucible with 42 per cent. of wrought iron scrap. By this means ferrous sulphide and a regulus of antimony are obtained, and the latter separates better from the slag if some dried sodium sulphate (10 parts) and charcoal powder (3 parts) are added before heating. These two substances form carbonic oxide and sodium sulphide, the latter then uniting with the ferrous sulphide to form an easily fusible slag.

Another method of extracting antimony consists in roasting the ore in a reverbatory furnace and then reducing the antimony oxide so formed with charcoal and sodium carbonate.

Antimony so prepared is never pure ; it usually contains lead, iron, and copper, and nearly always traces of arsenic, from which it must be completely purified before it can be employed for pharmaceutical preparations, such as tartar emetic, antimony chloride and oxide.

Crude antimony is purified by fusing 16 parts of it with 2 parts of dry sodium carbonate and 1 part of antimony trisulphide in a Hessian crucible for one hour. The regulus so obtained is then again fused for the same length of time with 1½ parts of sodium carbonate, and finally a third time with 1 part of sodium carbonate and a little nitre. The arsenic which was not converted in the first fusion into sodium sulpharsenite is oxidized to potassium arsenate by the nitre, leaving the antimony then free from arsenic.

Antimony remains unaltered when exposed to dry air. When small quantities are heated on charcoal before the blowpipe to above its boiling-point antimony burns, forming white fumes of antimonous oxide which are partly deposited on the charcoal. If the

fused metal is then allowed to cool it becomes covered with a network of transparent crystals of the oxide.

Powdered antimony burns brilliantly in chlorine gas, forming one of its chlorides. It also unites directly with sulphur.

Hydrochloric or dilute sulphuric acid has no action on antimony; nitric acid easily oxidizes it to one of the oxides of antimony, forming a white powder insoluble both in water and nitric acid. Aqua regia alone dissolves it, producing either the tri- or pentachloride. Both these chlorides dissolve in hydrochloric acid, but are precipitated by water as oxychlorides. Tartaric acid prevents the precipitation of these oxychlorides.

Antimony is used for many other purposes besides the preparation of useful medicines. It enters into the composition of some important alloys, such as *type-metal* (antimony, lead, and tin) and *Britannia-metal* (antimony, tin, and zinc).

ANTIMONIURETTED HYDROGEN (Stibine).

Composition : SbH_3.

This gaseous compound very closely resembles the corresponding arseniuretted hydrogen, but is less poisonous. Antimoniuretted hydrogen is prepared, in the same way as the arsenic compound, from an alloy of antimony and zinc, or better, by acting upon a compound of antimony and potassium with dilute sulphuric or hydrochloric acid. It is, further, always produced when nascent hydrogen comes into contact with a soluble antimony compound in an acid solution.

Antimoniuretted hydrogen is a colourless gas without odour, is decomposed at a low red heat, and burns in the air with a greenish flame, forming antimonous oxide and water. A piece of cold white porcelain depressed on this flame receives a black stain of free antimony. We have already described how this antimony stain may be distinguished from a corresponding one of arsenic (p. 241). It may be mentioned that when antimoniuretted hydrogen is passed into a solution of silver nitrate a black precipitate of a compound of silver and antimony is formed, while arseniuretted hydrogen under the same conditions precipitates metallic silver and the arsenic becomes oxidized to arsenious acid.

OXIDES AND OXY-ACIDS OF ANTIMONY.

Two compounds of antimony and oxygen are known, resembling in composition the two oxides of arsenic—viz. antimony trioxide, or antimonous anhydride (Sb_4O_6), corresponding to arsenious anhydride (As_2O_3), and antimonic anhydride (Sb_2O_5), corresponding to arsenic anhydride (As_2O_5). Besides these, a third compound also exists, having the composition: Sb_2O_4, which may, however, be considered as a compound of the other two, thus: Sb_2O_3, Sb_2O_5 or $(SbO_2)O(SbO)$.

Antimony is more electropositive than arsenic, and antimony trioxide is in fact more of a base than an acid, but is so weak a base that its compounds with acids are immediately decomposed by water.

ANTIMONY TRIOXIDE.

Composition: Sb_4O_6.

This compound occurs in nature in two distinct crystalline forms. Firstly, as rhombic prisms in the mineral *valentinite*, and secondly, in regular octahedra as *senarmontite*. Both forms may be obtained by burning antimony in the air and condensing the white vapours on a cold body. Both are isomorphous with the two forms in which arsenious anhydride crystallizes, and the two substances are therefore said to be *isodimorphous*.

In the wet way antimony trioxide may be obtained by acting upon finely powdered antimony with dilute nitric acid, or by precipitating a solution of antimony trichloride with water and washing the white oxychloride with sodium carbonate, when white insoluble antimony trioxide remains behind.

The dried oxide becomes yellow when heated but is again colourless when cold; when more strongly heated it melts, and at still higher temperatures it sublimes, taking up oxygen from the air and becoming converted into antimony tetroxide.

Antimony trioxide is insoluble in nitric acid and in dilute sulphuric acid, but is dissolved by hydrochloric acid, concentrated sulphuric acid,[1] or tartaric acid, as well as by acid potassium tar-

[1] From the solution of antimony trioxide in concentrated sulphuric acid the salt, *antimonous sulphate*: $(SO_2)_3O_6Sb_2$, in which the oxide is a base, crystal-

trate. In the last case a soluble crystalline compound is formed, called *tartar emetic*—potassium antimony tartrate.

With strong bases antimony trioxide behaves as an acid. It dissolves, for example, in strong caustic soda, and the solution on cooling deposits crystals of sodium antimonite, of the composition: $SbO{\cdot}ONa + 3H_2O$. In most of its compounds the trioxide takes the form of the monad radical: SbO.

The compound obtained on precipitating antimony trichloride with sodium carbonate is not antimony carbonate but simply the hydrated trioxide, which loses its water on boiling. Antimony trioxide is too weak a base to combine with carbonic acid.

ANTIMONIC ANHYDRIDE. (**Antimony Pentoxide.**)

Composition: Sb_2O_5 or $(SbO_2)_2O$.

Antimonic anhydride, obtained by gently heating either of the antimonic acids, is a bright yellow powder insoluble in water, and which when strongly heated does not melt but decomposes into antimony tetroxide and free oxygen.

Corresponding to this compound are three antimonic acids.

Ortho-antimonic Acid: H_3SbO_4, was obtained by Geuther by precipitating a solution of potassium antimonate, $KSbO_3$, by dilute nitric acid, washing the precipitate, and allowing it to stand for several months.

Antimonic Acid: $SbO_2{\cdot}OH + H_2O$, is a white powder, which, though scarcely soluble in water, reddens litmus paper. It may be obtained by acting on powdered antimony with aqua regia containing an excess of nitric acid, or by heating the metal for a long time with strong nitric acid. On heating a mixture of powdered antimony with four times its weight of nitre a deflagration takes place and the saline mass, when afterwards extracted with lukewarm water, leaves a white powder of potassium antimonate: $SbO_2{\cdot}OK$. This compound is only slightly soluble in cold water and can only be slowly dissolved by continued boiling. If the solution so obtained is then evaporated, the salt remains behind as a gummy

lizes out. This salt is decomposed by water into free sulphuric acid and basic sulphates.—ED.

mass. Nitric acid decomposes it, giving a white precipitate of antimonic acid.

This form of antimonic acid is soluble in concentrated hydrochloric acid, and easily soluble in caustic potash, but it is not dissolved by ammonia. Its salts, even those of the alkalies, are mostly insoluble or difficultly soluble in water and are easily decomposed even by weak acids.

Metantimonic Acid :[1] $H_4Sb_2O_7 = O\left\{\begin{matrix} SbO(OH)_2 \\ SbO(OH)_2 \end{matrix}\right.$

This tetrabasic acid resembles the preceding monobasic acid in its external properties ; it is, however, more soluble in water and acids and in ammonia. It is formed when antimony pentachloride is decomposed by water :—

$$2SbCl_5 \quad + \quad 7H_2O \quad = \quad H_4Sb_2O_7 \quad + \quad 10HCl,$$

or by acting on a metantimonate with hydrochloric acid. In both cases it separates as an amorphous precipitate. In combination with potassium it may be easily obtained by fusing ammonium or potassium antimonate with three times its weight of caustic potash. The saline mass is then dissolved in water and evaporated down, when potassium metantimonate separates out as deliquescent crystals on cooling. A small quantity of cold water decomposes this—the normal salt—into free alkali and the diacid compound ($H_2K_2Sb_2O_7 + 6H_2O$) which remains behind as a granular mass. Hydrochloric acid separates metantimonic acid from both salts.

Metantimonic acid possesses the remarkable property of forming a compound with sodium insoluble in water. If a solution of sodium chloride or of any other sodium salt is added to the above-named solution of potassium metantimonate, containing free alkali, a white precipitate of sodium metantimonate is formed. On account of this reaction potassium metantimonate is sometimes used as a reagent for sodium compounds. It is not, however, much employed for this purpose, as the solution of the potassium salt gradually changes into the ordinary antimonate, which does not produce an insoluble salt with sodium compounds.

[1] By analogy with the acids of phosphorus, this acid should be called pyrantimonic acid and the preceding compound metantimonic acid. The names given above are those in general use among chemists.—ED.

Antimony Tetroxide: $Sb_2O_4 = (SbO_2)O(SbO)$, is a white powder which becomes yellow when heated, but neither melts nor sublimes. It is formed when either antimony trioxide or antimonic anhydride is heated to redness in the air, the former compound then taking up oxygen and the latter losing it. When fused with caustic potash or potassium carbonate, potassium antimonoso-antimonate, $Sb_2O_4 \cdot K_2O$, is formed.

COMPOUNDS OF ANTIMONY WITH THE HALOGENS.

The haloid compounds of antimony correspond to those of phosphorus. Two chlorides are known—viz. the tri- and penta-chlorides—both of which, like the chlorides of phosphorus, are decomposed by water into hydrochloric acid and the corresponding oxygen compounds. An antimony compound corresponding to phosphoric oxychloride with the composition $SbOCl_3$ has not yet been prepared, but a similar compound of triad antimony—antimonous oxychloride: SbOCl—is known.

Antimony Trichloride (Antimonous Chloride): $SbCl_3$.

This compound, sometimes called *butter of antimony* from its consistency, is a soft white, crystalline solid, which melts at 73°, boils at 223°, and deliquesces in moist air.

It may be prepared by heating an excess of finely powdered antimony in chlorine gas, or by distilling an intimate mixture of 1 part of powdered antimony with 3 parts of mercuric chloride. The usual method of preparation is to dissolve antimony trisulphide in strong hydrochloric acid, evaporate the solution to drive off the water and excess of acid, and then to distil the residue. As soon as the distillate begins to solidify the receiver is changed, and by again distilling those portions which come over last, the compound is obtained pure.

Antimony trichloride unites with some metallic chlorides to form crystalline double chlorides—*e.g.* sodium antimony chloride: $3NaCl,SbCl_3$. It dissolves in hydrochloric acid or in a small

quantity of water; the addition of a large quantity of water to either solution produces a white precipitate of antimony oxychloride (algaroth powder). Tartaric acid prevents this precipitation.

Algaroth powder is a white amorphous substance insoluble in water. It contains antimony, oxygen, and chlorine, but has no definite composition. By boiling with water it gives up some chlorine, and when boiled with sodium carbonate is converted into antimonous acid.

Antimony Pentachloride (Antimonic Chloride): $SbCl_5$.

Unlike phosphorus pentachloride, the antimony compound is not a solid substance, but a pale yellow liquid, fuming in the air. Under reduced pressure it may be distilled unchanged, but when distilled at the ordinary pressure, it undergoes partial decomposition into chlorine and antimony trichloride, and does not, therefore, possess any constant boiling point.

Antimony pentachloride is obtained either by saturating the trichloride with chlorine, or by passing a rapid stream of chlorine over heated antimony. It attracts moisture from the air, and then solidifies to a crystalline mass. In a small quantity of water it dissolves to a clear solution, which, on standing over sulphuric acid, deposits crystals of a hydrate having the composition $SbCl_5 + 4H_2O$. Excess of water precipitates metantimonic acid, but tartaric acid prevents the precipitation. If, however, its acid solution is mixed at once with a large quantity of water, the liquid remains clear.

The two atoms of chlorine which antimony pentachloride contains in excess of the trichloride are only feebly united, and it is therefore well adapted for imparting chlorine to many substances —*e.g.* carbonic oxide, ethylene, and other organic compounds. With dry sulphuretted hydrogen the pentachloride is converted into hydrochloric acid and *antimony sulphochloride*, $SbSCl_3$, a white crystalline, easily fusible substance.

Antimony Tribromide: $SbBr_3$, which may be obtained by the direct union of its constituents, is a solid crystalline mass, melting at 93°, boiling at 280°, and subliming in colourless needles. The pentabromide has not yet been prepared.

Antimony Triiodide : SbI_3, sublimes in large red crystals, which become darker when fused.

COMPOUNDS OF ANTIMONY WITH SULPHUR.

Two of these compounds are known—viz. the trisulphide and the pentasulphide. They correspond in composition to the two oxides, and closely resemble one another both in their external and in their chemical properties. Both are insoluble in water, and both unite with strong bases to form sulphosalts.

Antimony Trisulphide (Antimonous Sulphide) : Sb_2S_3, occurs in nature as the mineral *grey antimony ore*, *stibnite*, or *antimonite*, and is the chief source of antimony and its compounds. It is found crystallized in long rhombic prisms or in fibrous crystalline masses of a dark grey colour with a metallic lustre. It easily fuses and re-solidifies to a crystalline mass, forming the crude impure sulphide of commerce (p. 251).

It may be artificially prepared by fusing together antimony and sulphur, and repeating the process several times with addition of sulphur, or by precipitating an acid solution of antimony trichloride with sulphuretted hydrogen. The trisulphide prepared in the wet way is an amorphous orange-coloured substance, which when fused and resolidified closely resembles the ordinary sulphide.

Antimony trisulphide is converted by nitric-acid into insoluble antimony trioxide or antimonic acid, while the sulphur partly separates in the free state and is partly oxidized to sulphuric acid. Hydrochloric acid easily dissolves it, forming antimony trichloride, with liberation of sulphuretted hydrogen. It combines easily with potassium or sodium sulphide to form a soluble sulphantimonite, from which hydrochloric acid again precipitates the orange coloured trisulphide. Caustic soda also dissolves it, and the solution then contains sodium antimonite as well as sodium sulphantimonite :—

$$2Sb_2S_3 + 4NaOH = \underset{\text{Sodium sulphantimonite}}{3SbS{\cdot}SNa} + \underset{\text{Sodium antimonite}}{SbO{\cdot}ONa} + 2H_2O.$$

Not only caustic soda but also sodium carbonate dissolves antimony trisulphide, and especially the orange-coloured, amorphous variety. The colourless solution when boiled with an excess of the trisulphide takes up still more of it, the greater portion of which is again deposited on cooling. This precipitate is not the pure sulphide, but contains varying quantities of sodium antimonite and antimony trioxide, and was previously used in medicine under the name of *kermes mineral*, or simply *kermes*. Ammonium carbonate does not dissolve antimony trisulphide, a property which serves to distinguish it from the trisulphide of arsenic.

If antimony trisulphide is heated (roasted) in the air, a portion is converted into sulphurous anhydride and antimony trioxide, the latter substance then combining with the undecomposed trisulphide to form a brownish vitreous, semi-transparent mass. This mixture of the trioxide and trisulphide, prepared in this and other ways, was formerly used in medicine and for the preparation of other antimony compounds under the names *antimony glass*, *crocus antimonii*, &c. It is now only employed for imparting a yellow colour to glass and porcelain.

Antimony Pentasulphide: Sb_2S_5, sometimes called 'the golden sulphide,' is a dark orange-coloured powder, and may be obtained by passing sulphuretted hydrogen through an acid solution of antimonic acid. It is, however, usually prepared by precipitating a solution of sodium sulphantimonate (Schlippe's salt) with dilute hydrochloric acid.

Antimony pentasulphide forms with alkaline sulphides a series of salts corresponding to a tribasic sulphantimonic acid. The best known and most stable of these is the sodium compound: $SbS\cdot(SNa)_3 + 9H_2O$, which is easily soluble in water, and from which it crystallizes in colourless tetrahedra. This salt, called *Schlippe's salt*, after its discoverer, is easily formed by boiling an aqueous solution of sodium sulphide with antimony trisulphide, and sufficient sulphur to convert it into the pentasulphide. Instead of sodium sulphide, caustic soda and sulphur may be used, which on boiling yield sodium sulphide and sodium thiosulphate, or, instead of caustic soda, sodium carbonate and slaked-lime. To prepare the compound 9 parts of crystallized sodium carbonate are boiled with 3 parts of slaked-lime, 3 parts of antimony trisulphide, 1 part of sulphur, and sufficient water. The hot liquid is rapidly filtered off from

the calcium carbonate and evaporated down until the salt crystallizes out. The crystals so obtained must be preserved in well-stoppered bottles, as the carbonic anhydride of the air decomposes them, forming sodium carbonate, sulphuretted hydrogen, and antimony sulphide. This causes the colourless, or, at most, pale yellow crystals to become gradually covered with an amorphous brown-coloured crust.

The potassium compound has a similar composition; aqueous solutions of these salts give with most other metallic salts insoluble precipitates of corresponding sulphantimonates. The copper compound, for example, has the composition: $(SbS)_2 (S_2Cu)_3$.

BORON.

Chemical Symbol: B.—*Atomic Weight*: 11.

Boron, like phosphorus, is only found in inorganic nature in combination with oxygen, either as the free compound—boric acid, or united with bases as various borates. The most important minerals containing boron are—*sassolite* (boric acid): $B(OH)_3$, *tinkal* or native borax: $Na_2B_4O_7 + 10H_2O$, *boracite*: $2Mg_3B_8O_{15} + MgCl_2$, *boronatro-calcite* (calcium and sodium borates), and *datolite* (calcium borate and silicate).

Boron can be easily prepared from anhydrous fused boric acid. This substance is coarsely powdered, mixed with small pieces of sodium (6 parts of sodium to 10 parts of boric acid), thrown into an iron crucible which has been previously heated to bright redness, and then covered with 5 parts of well-dried common salt. As soon as the reaction in the closed crucible is over its contents are stirred with an iron rod and poured, while still fluid and red-hot, into dilute hydrochloric acid, in which everything dissolves except the boron which has been set free by the sodium. The residue is brought on a filter, washed, first with dilute hydrochloric acid, then with cold water, and dried at the ordinary temperature on a porous slab, or over sulphuric acid.

Boron obtained in this way is an amorphous olive-green powder, tasteless, and without odour, and a non-conductor of electricity. It is extremely infusible. Water, even at its boiling point, does not

attack it; nor is it acted upon by hydrochloric acid. It is oxidized, however, to boric acid by nitric acid, aqua regia, or concentrated sulphuric acid, as well as when heated in steam or when fused with caustic soda. When heated in the air it burns easily, producing boric anhydride; in oxygen it burns with a brilliant light of a greenish colour. It also burns in chlorine, producing boron trichloride. Boron unites readily with nitrogen; when heated in this gas to redness it forms a very stable nitride.

Boron can also be obtained in a crystalline form by dissolving amorphous boron in fused aluminium. Amorphous boron is stamped tightly in a Hessian crucible, and a hole made in the middle, in which is placed a rod of aluminium. After the crucible has been closed, it is placed inside a second large crucible, and the space between them filled up with powdered charcoal; the lid of the exterior crucible is then cemented with clay, and the whole heated to bright redness for two hours. On cooling, the surface of the aluminium is found covered with crystals of boron. The aluminium is dissolved by dilute hydrochloric acid, and the crystalline boron then remains, partly as dark brown translucent, and partly as transparent yellowish crystals of specific gravity $= 2 \cdot 6$, mixed with thin, opaque, six-sided, tabular crystals of a compound of aluminium and boron, which may be easily removed by washing. (See Appendix.)

Another kind of crystalline boron distinguished by its great hardness is obtained by strongly heating a mixture of boric anhydride and aluminium in a carbon crucible, air being excluded as much as possible. These crystals, which approach the diamond in brilliancy and hardness, are not, however, pure boron, but contain 4 per cent. of carbon and 6·7 per cent. of aluminium.

No practical use has yet been discovered for boron. No compound with hydrogen has yet been obtained in pure condition, and in general the number of the boron compounds is small. By far the most important compound is boric acid, in which, as in all other compounds, boron plays the part of a triad element.

BORIC ANHYDRIDE : B_2O_3, and BORIC ACID : $B(OH)_3$.

Boric acid crystallizes in colourless lustrous tablets, with a faint acid taste. It is soluble in water, especially when warm, and also dissolves in alcohol. One part of boric acid dissolves in three parts of water at 100°, but requires twenty-five parts at 19°. A hot saturated solution deposits therefore nearly all the boric acid on cooling. The aqueous solution possesses both a faint acid and an alkaline reaction; it reddens blue litmus paper, and at the same time turns yellow turmeric paper brown.

Boric acid occurs in such large quantities free in nature that, until quite recently, other naturally occurring boron compounds have been but little used for the preparation of the acid and its salts. In some parts of Tuscany jets of steam (called *suffioni*, or *fumaroli*) issue from the ground, which then condense to form bogs or marshes (*lagoons*). This steam carries with it small quantities of boric acid, and although the condensed water rarely contains more than $\frac{1}{10}$ per cent. of the compound, many hundredweights of boric acid are annually prepared from this source.

The places where these jets of steam issue from the earth, or where they have been artificially produced by boring, are built round so as to form a large basin, which is then filled with water. The water is soon raised to boiling by the condensed steam, from which it abstracts the boric acid. After a certain time the water is allowed to flow into a second somewhat lower basin where it receives fresh quantities of boric acid, while the first basin is again filled with fresh water. When the water has, in this way, passed through four or more basins, from each of which it has received boric acid so that it contains about one per cent., the suspended impurities are allowed to settle and the liquid evaporated down to crystallize. For this purpose it is run into shallow pans heated from beneath by other similar jets of steam. And in this way the use of fuel, which it is difficult to procure in the district, is entirely avoided. The boric acid which separates out on cooling the solution, when sufficiently concentrated, is contaminated with various impurities, especially with ammonium and calcium sulphates. It is purified by recrystallization.

Similar steam-springs containing boric acid are also met with in other volcanic districts, for example in the Lipari Islands.

Recently considerable quantities of boric acid have been discovered in California, whence most of the American acid is now derived.

Several hypotheses have been proposed to explain the occurrence of boric acid in these hot springs; it is most probable that the acid is produced by the action of steam on boron nitride, which is then decomposed into boric acid and ammonia. Ammonium compounds are always present in the hot springs.

The extraction of boric acid from native borax (tinkal) and from other boron minerals, especially boronatro-calcite and borocalcite, consists simply in decomposing them with hot hydrochloric acid and purifying the boric acid which separates out on cooling by re-crystallization.

Although boric acid is only slightly volatile even at high temperatures, we have seen that it passes off with the steam when its aqueous solution is boiled. Even when its alcoholic solution is boiled considerable quantities are carried off with the alcohol vapour, which then burns with a bright green flame when ignited. This colour is, however, only imparted to the flame of the burning alcohol by free boric acid, not by its salts. Alcohol, if poured on sodium borate or any other salt of boric acid and ignited, burns with a yellow flame; but the addition of a drop of concentrated sulphuric acid sets the boric acid free, and the flame changes at once to a bright green.

When heated to 100° ordinary boric acid: $B(OH)_3$, loses water and changes into *metaboric acid*, a white powder of the composition: $BO \cdot OH$; by heating to 150°—160° in a stream of dry air a further quantity of water is lost and an acid of the composition: $H_2B_4O_7$, *pyroboric acid*, remains. Heated still more strongly, boric acid froths up, and at red-heat melts to a clear viscid liquid, consisting of boric anhydride, which solidifies to a hard transparent brittle glass. On standing in the air, boric anhydride gradually becomes opaque owing to the absorption of water, for which it possesses considerable attraction.

Boric acid is a weak acid, as is shown by its behaviour with litmus and turmeric. It combines easily with the alkalies to form salts soluble in water; the other borates are difficultly soluble in water, but easily soluble in acids.

The constitution of the borates is usually somewhat complex Compounds are known of the ordinary tri-basic acid, $B(OH)_3$, particularly organic salts, in which the three hydrogen atoms are dis-

placed by compound radicals. Salts have also been prepared from the mono-basic metaboric acid : $BO \cdot OH$, in which the one atom of hydrogen is displaced by an atom of a monad metal. Most of the borates, including the commonest—sodium borate or borax—have, however, a more complex composition, and correspond to the dibasic pyroboric acid, $H_2B_4O_7$—*e.g.* $Na_2B_4O_7$, and CaB_4O_7.

The constitution of these pyroborates may be represented in various ways. Formerly it was considered that borax, which may be taken as representing this class, was a double compound of sodium metaborate with boric anhydride : $2BO \cdot ONa + B_2O_3$. A more probable formula is : $O\begin{cases} B_2O_2 \cdot ONa \\ B_2O_2 \cdot ONa \end{cases}$, or, possibly, a portion of the boron may be present as acid, and a portion as base ; but until our knowledge is further advanced no constitutional formula can be given with certainty.

Boric acid, like all weak acids, can unite with strong acids, and forms compounds with sulphuric and phosphoric anhydrides having the respective composition : B_2O_3,SO_3 and B_2O_3,P_2O_5, in which the boric acid plays the part of a base.

The chief use of boric acid is for the preparation of borax. It is an excellent antiseptic, and has been considerably used for this purpose in recent years. Whether, however, large quantities of boric acid can be taken into the system without injurious effects remains as yet doubtful.

OTHER COMPOUNDS OF BORON.

Boron Trichloride : BCl_3.—This compound is produced when boron is heated in gaseous chlorine, or by strongly glowing an intimate mixture of boric anhydride and charcoal in a porcelain tube through which a stream of dry chlorine is passed. The reaction which then goes on is expressed by the following equation :—

$$B_2O_3 \quad + \quad 3C \quad + \quad 3Cl_2 \quad = \quad 2BCl_3 \quad + \quad 3CO.$$

The gaseous products are led through a U-tube surrounded by a freezing mixture, in which the boron trichloride condenses to form a colourless liquid, boiling at 17°, and having a specific gravity

of 1·35. This liquid fumes strongly in the air, and is rapidly decomposed by water into boric and hydrochloric acids. Boron trichloride unites with ammonia to form a solid white crystalline compound of the composition: $2BCl_3,3NH_3$. This compound, when heated, sublimes, and is decomposed at once by water into boric acid, hydrochloric acid, and ammonium chloride.

Boron Tribromide: BBr_3, is a colourless liquid, boiling at 90°, and with similar properties to the chloride.

Boron Trifluoride: BF_3.—This body, unlike the two other corresponding compounds, is a colourless gas, and can only be condensed to a liquid with difficulty. It possesses a piercing suffocating odour, fumes strongly in the air, and on account of its strong attraction for water, chars many organic substances like concentrated sulphuric acid. It is extremely soluble in water, one volume of this liquid dissolving 700 to 1,000 volumes of the gas. The gas may be obtained by heating an intimate mixture of 1 part of boric anhydride (or 2 parts of anhydrous borax) with 2 parts of fluor-spar and 12 parts of concentrated sulphuric acid in a glass flask. The change which then takes place is as follows:—

$$B_2O_3 + 3CaF_2 + 3SO_2(OH)_2 = 3SO_2{\cdot}O_2Ca + 2BF_3 + 3H_2O.$$

The large excess of sulphuric acid is required to absorb the water produced in the reaction. Boron trifluoride may also be prepared from boric anhydride and fluor-spar without sulphuric acid if a mixture of these two substances is heated to bright redness in an iron tube, the calcium then remaining behind as calcium borate:—

$$2B_2O_3 + 3CaF_2 = 2BF_3 + B_2(O_2Ca)_3.$$

On evaporating an aqueous solution of the fluoride, boric acid separates out, and a monobasic acid remains, of the composition: HBF_4 or HF,BF_3—*fluoboric acid*—which may be considered as a double compound of hydrofluoric acid and boric fluoride. The same substance is also more easily obtained by dissolving boric acid in hydrofluoric acid.

Fluoboric acid cannot, however, be obtained in the pure state. (See Appendix.) If the aqueous solution is concentrated by evaporation, hydrofluoric acid is evolved. Its salts, having the general composition: $M'BF_4$ (where M' is a monad metal), are mostly soluble in water, the most insoluble being the potassium

compound: KBF_4. On mixing aqueous fluoboric acid with a solution of a potassium compound, a gelatinous precipitate of potassium fluoborate is formed, which becomes a white powder when dried. From a hot saturated solution in water, the salt separates out on cooling in brilliant crystals.

Boron Sulphide: B_2S_3, is a white, vitreous solid, of piercing odour, which can be fused in a stream of hydrogen. It is produced by heating amorphous boron in sulphur vapour or in sulphuretted hydrogen, and then condenses in a well-cooled receiver. Water easily decomposes it into boric acid and sulphuretted hydrogen.

Boron Nitride: BN.—Boron is one of the few elements that unite directly with nitrogen. The nitride is formed when amorphous boron is heated in a stream of nitrogen or ammonia, also when a mixture of boric anhydride and charcoal is strongly heated in a stream of nitrogen, or by glowing a mixture of dried borax and ammonium chloride. By digesting the residue obtained in the last method with dilute hydrochloric acid, the nitride remains as a white amorphous powder. Boron nitride is a stable compound, and remains unchanged when boiled with water or when glowed in the air or in hydrogen. It is, however, decomposed into boric acid and ammonia when heated to low redness in a current of steam; the same change is produced by fusion with caustic potash.

SILICON.

Chemical Symbol: Si.—*Atomic Weight*: 28·3.

Silicon occurs most abundantly and is widely distributed in nature, but never in the free state. It is always found, like phosphorus and boron, united with oxygen. Its only oxide, silica, is known both free and in combination with bases as innumerable minerals. Considering the wide distribution and great variety of the silicates, it may be asserted that silicon plays the same part in inorganic as carbon does in organic nature. Both are tetrad elements in almost all their compounds.

Silicon may be separated from silica by potassium, but the decomposition is always incomplete, and the product therefore impure. It is better to employ a compound of silicon fluoride with potassium or sodium fluoride—potassium or sodium fluosilicate: K_2SiF_6—which can be readily obtained in the pure state. A mixture of one of these salts with sodium chloride and metallic sodium cut into small pieces is thrown into a red-hot iron crucible, which is then closed and kept for a short time at a low red heat. After cooling, the contents of the crucible are boiled with dilute hydrochloric acid. By this process fluorine is abstracted by the sodium from the double fluoride and silicon set free.

Amorphous silicon prepared in this way is a dark brown powder, insoluble in water and in nitric or sulphuric acid. Aqueous hydrofluoric acid dissolves it with evolution of hydrogen, and it also decomposes strong caustic potash, forming potassium silicate. Heated in the air it burns easily with a bright light, to form silica; the combustion, however, is only incomplete, as the silica is fused by the high temperature, and so protects a portion of the silicon from the air. When heated in a stream of hydrochloric acid gas this form of silicon takes up three atoms of chlorine and one of hydrogen, and becomes converted into the substance called silicochloroform: $SiHCl_3$ (see sequel). If amorphous silicon is strongly heated in a crucible out of access of air, it contracts considerably, becomes of a chocolate brown colour, and now no longer catches fire when heated in the air. It has also lost its property of dissolving in hydrofluoric acid or in caustic potash after this treatment.

Silicon may be prepared in the crystalline form by fusing aluminium with thirty times as much sodium fluosilicate. The black residue which remains is then treated first with concentrated hydrochloric acid to remove the aluminium, and then with hydrofluoric acid. Another and simpler method of preparing crystalline silicon consists in throwing a mixture of three parts of potassium fluosilicate, one part of sodium in small pieces, and one part of granulated zinc, into a red-hot Hessian crucible, and then heating for some time to such a temperature that the zinc remains fused, but is not volatilized. The zinc regulus, which contains the silicon, is afterwards removed from the crucible, thoroughly boiled with water to remove the slag, and then the zinc dissolved out with hydrochloric acid.

Crystalline silicon prepared in either of these ways consists either of opaque, lustrous tablets of a dark grey colour, resembling

graphite, or else of brilliant prismatic crystals which consist of an aggregation of octahedra and tetrahedra, and possess an iron grey colour and considerable hardness. Silicon is thus isodimorphous with carbon. The specific gravity of crystalline silicon is 2·2 to 2·5; it is a conductor of electricity, and remains unaltered when heated in the air, but melts at high temperatures. It is neither attacked by nitric nor by hydrofluoric acid, but dissolves when heated with strong caustic potash, with evolution of hydrogen, and burns in chlorine to silicon tetrachloride.

COMPOUNDS OF SILICON.

Silicon unites directly with oxygen and with the halogens to form compounds, in which it exists as a tetrad element. An oxide of silicon corresponding to carbonic oxide, with the composition: SiO, has not yet been prepared. (See Appendix.) Otherwise its compounds are similar to those of carbon, although the similarity is more in their composition than in their properties. The following pairs of compounds correspond to one another:—

Silica	SiO_2	Carbonic acid . . .	CO_2
Silicon hydride . .	SiH_4	Methane (marsh-gas) .	CH_4
Silicon tetrachloride .	$SiCl_4$	Carbon tetrachloride .	CCl_4
Silicon hexachloride .	Si_2Cl_6	Carbon hexachloride .	C_2Cl_6
Silicon sulphide . .	SiS_2	Carbon sulphide . .	CS_2
Silicochloroform .	$SiHCl_3$	Chloroform . .	$CHCl_3$
Silicoiodoform . .	$SiHI_3$	Iodoform	CHI_3
Silicoxalic acid .	$\begin{cases} SiO{\cdot}OH \\ SiO{\cdot}OH \end{cases}$	Oxalic acid . .	$\begin{cases} CO{\cdot}OH \\ CO{\cdot}OH \end{cases}$

SILICA (SILICIC ANHYDRIDE): SiO_2, and SILICIC ACID.

Silicon forms only one oxide—silicic anhydride—or, as it is briefly called, silica. This united in varying proportions with water forms different varieties of silicic acid.

Free silica occurs in nature both crystalline and amorphous. In the crystalline form chiefly as *quartz* or *rock crystal*, in six-

sided prisms bounded at the ends by similar pyramids, and belonging therefore to the hexagonal system. Quartz in its purest form is transparent and colourless, but is frequently coloured brownish or violet—in the former case it is known as *smoky-quartz*, in the latter as *amethyst*. Ordinary *sand* consists of particles of silica, which when united together by some cementing substance constitute the different varieties of *sandstone*. Quartz is also contained in the free state in many important rocks—*granite*, for example, is made up of separate crystals of quartz, felspar, and mica. The specific gravity of this form of silica is 2·65.

Crystalline silica is also found in some rocks in minute crystals belonging to the rhombic system, and has a specific gravity of 2·31, or lower than that of quartz. This variety, which is called *tridymite*, appears to be the most stable form of silica at a red-heat, as both quartz and amorphous silica pass into it when strongly heated.

Besides these two crystalline forms, silica is also found in nature, usually in combination with water, in the amorphous state. The minerals *agate*, *chalcedony*, *opal*, *jasper*, *flint*, consist of amorphous silica mixed to some extent with the crystalline modification. Some of these—*e.g.* opal—are of attractive colours and are used as jewels. Agate and chalcedony are celebrated for their extreme hardness, and are highly valued for the manufacture of mortars. The *siliceous sinter*, deposited during the evaporation of the water from siliceous springs, and the so-called *infuscrial earth*, or the inorganic remains of certain infusoria, consist essentially of amorphous silica. This infusorial earth—*Kieselguhr* of the Germans—occurs largely in certain localities in North Germany and in North Scotland as a light, extremely fine powder, mostly of a yellow colour. It is used for many technical purposes, especially for mixing with nitro-glycerine to form dynamite.

Silica is likewise found in the animal and vegetable kingdoms. The glassy coating of the stems of certain grasses and other allied plants, cereals, rushes, and especially of the Equisetaceae (horse-tails) consist essentially of silica. The ashes of the feathers of many birds contain as much as 40 per cent. of silica.

Much more widely distributed in the mineral kingdom than silica are its compounds with various bases, called silicates, and of which the greater part of the solid crust of the earth consists. Among these the different felspars, double silicates of aluminium and potassium or sodium, together with the clays, schists, &c., produced from them, take the first place.

The properties of the various modifications of silica differ in many respects. All are insoluble in water and in nitric, hydrochloric, or sulphuric acid, as well as in aqua regia, but dissolve in hydrofluoric acid, and possess in general none of the properties of an acid. They remain unchanged at the highest temperatures of our furnaces, but melt in the oxy-hydrogen flame and form a clear transparent glass on cooling. The quartz modification is very hard—it easily scratches glass—but the amorphous form is much softer. The specific gravity of the former is 2·65, that of the latter 2·20; the specific gravity of both changing to 2·31 when strongly glowed, owing to the conversion into tridymite. Crystalline silica is scarcely attacked even by boiling aqueous caustic potash or soda, but when fused with an excess of either of these substances in the solid form, or with their carbonates, silicates soluble in water are produced (water-glass). Amorphous silica is dissolved more or less readily by aqueous alkalies; infusorial earth is very readily dissolved.

If a concentrated aqueous solution of an alkaline silicate prepared by either of the above-mentioned methods is mixed with hydrochloric acid, the silicic acid separates out as a gelatinous mass, and the whole liquid becomes so viscid that the vessel may be inverted without anything running out. This silicic acid is soluble in water, especially in the presence of hydrochloric acid, for if the solution of the silicate is sufficiently dilute, hydrochloric acid produces no precipitate. It is this silicic acid which is contained in the water of siliceous springs, and which is deposited as siliceous sinter on evaporation.

Pure amorphous silica, as a light, finely divided powder, may be easily obtained by the decomposition of silicon fluoride with water (p. 275).

If this gelatinous soluble silicic acid is evaporated to *complete* dryness on a water-bath, it loses its water, and there remains amorphous silica, which is no longer soluble in water or hydrochloric acid, but which easily dissolves on warming in aqueous caustic soda or in sodium carbonate. When heated to redness it is no longer soluble in aqueous alkalies, and can now only be converted into soluble water-glass by fusion with caustic alkalies or alkaline carbonates.

Corresponding to these differences in solubility of the various forms of silica are differences in the readiness with which the various silicates are decomposed. Those which are poor in silica,

especially those containing water (the zeolites), when finely divided, are decomposed by hydrochloric acid. Those, on the other hand, which contain more silica—*e.g.* the felspars—withstand the action of strong hydrochloric acid, and can be only brought into solution by treatment with hydrofluoric acid or by fusion with sodium (potassium) carbonate in a platinum crucible. In the latter case an alkaline silicate soluble in water is produced, and the bases which were previously united with the silica—*e.g.* lime, alumina, iron—are converted either into carbonates or into oxides soluble in acids. The fused mass, when cold, is digested with water and hydrochloric acid added to slight excess, when a clear solution is obtained as soon as the carbonic acid has been expelled by warming. If the quantity of water used was small, the solution will contain gelatinous flocks of silicic acid. The liquid is next evaporated to complete dryness, and best heated for a short time to about 120°, to render the silica completely insoluble, afterwards moistened with strong hydrochloric acid to bring into solution any oxychlorides which might have been formed during evaporation (*e.g.* of iron or aluminium), and finally extracted with hot water. In this way everything goes into solution except the silica, which can be easily separated by filtration, washed and weighed, while the bases in the filtrate can be estimated by any known method.

It is difficult to obtain a *silicic acid* of definite composition. If the gelatinous hydrate is dried over concentrated sulphuric acid, a transparent vitreous mass is obtained, of which the composition is approximately represented by the formula : $SiO(OH)_2$—*i.e.* a dibasic acid corresponding to the hypothetical sulphurous acid. Tetrabasic silicic acid of the composition : $Si(OH)_4$ has not yet been prepared. We know, however, from the composition of numerous silicates that salts of both these acids exist, as well as compounds of a dibasic disilicic acid of the possible formula : $O\left\{\begin{matrix}SiO\cdot OH\\SiO\cdot OH\end{matrix}\right.$

To the salts of the dibasic acid may possibly belong the mineral *wollastonite* : $SiO\cdot O_2Ca$, to those of the tetrabasic acid, *olivine* : $Si(O_2Mg)_2$. And a combination of the dibasic and tetrabasic acids may represent *serpentine* : $\left.\begin{matrix}SiO\\Si\end{matrix}\right\}(O_2Mg)_3$. (See Appendix.)

Similarly, those silicates containing three atoms of silicon—the trisilicates—may be considered as compounds of two of these acids

united together. *Orthoclase* (potash felspar : $KAlSi_3O_8$) would thus be a compound of dibasic silicic acid and disilicic acid :—

$$O\left\{\begin{array}{l}SiO\cdot O\\ SiO\cdot O\end{array}\right\}Al \qquad SiO\left\{\begin{array}{l}O\\ O\cdot K,\end{array}\right.$$

and *prehnite* : $Al_2Ca_2Si_3O_{11}$, a compound of tetrabasic silicic acid and of a hexabasic disilicic acid of the hypothetical constitution : $O\left\{\begin{array}{l}Si(OH)_3\\ Si(OH)_3\end{array}\right.$—*i.e.* its formula would become :—

$$O\left\{\begin{array}{l}Si\\ Si\\ Si\end{array}\right\}\begin{array}{l}(O_3Al)_2\\ (O_2Ca)_2\end{array}$$

It must be distinctly understood that these formulæ are not the symbolic expression of established facts, but only represent an attempt to give a simple explanation of the very various and often complex composition of the silicates. The chemical *constitution* of these compounds cannot be deduced simply from the results of analysis, but require extended researches similar to those which are necessary to establish the constitution of any chemical compound.

SILICON HYDRIDE.

Composition : SiH_4.

This compound is a colourless combustible gas, insoluble (or nearly so) in water. It may be obtained by acting upon magnesium silicide with dilute hydrochloric acid :—

$$SiMg_2 \quad + \quad 4HCl \quad = \quad 2MgCl_2 \quad + \quad SiH_4.$$

This magnesium silicide ($SiMg_2$) is prepared by throwing a mixture of 8 parts of anhydrous magnesium chloride, 7 parts of sodium fluosilicate, 2 parts of sodium chloride, and 4 parts of sodium in small pieces into a red-hot Hessian crucible, which is at once closed. The crude compound thus obtained always contains free magnesium, whence it follows that the silicon hydride prepared from it is always mixed with free hydrogen. In this state silicon hydride catches fire spontaneously in the air,

burning with a luminous flame to form silica and water. If a clean porcelain dish is depressed on the flame, brown amorphous silicon is deposited on it. Excluded from the air and heated to faint redness, the gas decomposes, like arsine and stibine, into amorphous silicon and free hydrogen.

The *pure* compound may be prepared by acting on an organic silicon compound of the composition: $SiH(OC_2H_5)_3$, with sodium. Four molecules of this compound are decomposed under the influence of the sodium, which remains itself unchanged, into one molecule of silicon hydride and three of the compound: $Si(OC_2H_5)_4$:—

$$4SiH(OC_2H_5)_3 = SiH_4 + 3Si(OC_2H_5)_4.$$

Silicon hydride burns easily in chlorine, producing hydrochloric acid and silicon tetrachloride. With caustic potash, it gives a silicate of potassium and free hydrogen:—

$$SiH_4 + 2KOH + H_2O = SiO(OK)_2 + 4H_2.$$

SILICON TETRACHLORIDE.

Composition: $SiCl_4$.

This, the best known chloride of silicon, is a colourless mobile liquid of 1·52 specific gravity and boiling at 58°. It fumes in the air, and is energetically decomposed by water into hydrochloric and silicic acids.

Silicon tetrachloride is obtained when amorphous silicon is heated in a stream of chlorine gas, or more readily by strongly heating an intimate mixture of silica and carbon in the same gas. A stiff dough is made of finely divided silica, powdered wood-charcoal, and starch paste, which is then formed into balls. These are allowed to dry in the air, and then heated to bright redness imbedded in charcoal powder. The porous mixture of silica and carbon so obtained is introduced while still hot into a dry porcelain tube, which can be heated to bright redness in a tube-furnace, while a current of dry chlorine passes through it. The reaction is expressed by the equation:—

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

The other end of the tube communicates air-tight with a

U-tube placed in a freezing mixture in which the silicon tetrachloride condenses, while the carbonic oxide and excess of chlorine are carried away to the open air. At the bottom of the U-tube is a small vertical tube (provided with a glass stopcock), through which the silicon tetrachloride can be drawn off into bottles or sealed tubes.

The corresponding *silicon tetrabromide*, $SiBr_4$, and the *tetriodide*, SiI_4, are prepared in exactly the same way as the chloride. The bromide is a colourless liquid, boiling at 153° and solidifying to a crystalline mass at −12°. The iodide is a crystalline solid, boiling at about 290°.

Silicon Hexachloride: Si_2Cl_6.—Besides the above-mentioned tetrachloride of silicon, a second compound—silicon hexachloride: Si_2Cl_6—is also known. This is also a colourless liquid, but has a specific gravity of 1·58, boils at 145°, and solidifies at about −4°. It is obtained by heating silicon in the vapour of silicon tetrachloride or by heating a mixture of silicon tri-iodide and mercuric chloride. At 350° it decomposes into the tetrachloride and free silicon, and this decomposition increases up to 800°. But at about 1,000° the hexachloride is again stable—*i.e.* silicon and the tetrachloride again unite to form the hexachloride. Water decomposes it into hydrochloric acid and disilicic or silico-oxalic acid: $\left\{\begin{array}{l}SiO\cdot OH\\SiO\cdot OH\end{array}\right.$

The corresponding *silicon hexiodide* is a crystalline solid, obtained by heating the tetriodide with finely divided silver. Silver iodide is then formed with the hexiodide.

SILICON FLUORIDE.

Composition: SiF_4.

This substance is a colourless gas, fuming strongly in the air, and with a suffocating odour. Its specific gravity is 3·6, and it is at once decomposed by water with separation of gelatinous silicic acid. It is produced when hydrofluoric acid acts upon silica in the presence of de-hydrating substances.

For its preparation a mixture of powdered fluor-spar and fine

dry sand, the latter in considerable excess (about equal parts), is heated in a thick glass flask with a large excess of concentrated sulphuric acid, so that a thin liquid of the consistency of cream is produced. Silicon fluoride is then evolved, according to the equation :—

$$SiO_2 + 2CaF_2 + 2SO_2(OH)_2 = SiF_4 + 2SO_2(O_2Ca) + 2H_2O,$$

while the water produced at the same time is absorbed by the excess of sulphuric acid. If the quantity of sand employed in the experiment is insufficient, the glass flask is strongly attacked by the hydrofluoric acid, and may be completely eaten through.

FLUOSILICIC ACID.

Composition : H_2SiF_6.

This dibasic acid, which may be considered as a double fluoride of silicon and hydrogen, is produced by the union of silicon fluoride with nascent hydrofluoric acid. These conditions are fulfilled when silicon fluoride comes into contact with water. Decomposition then occurs according to the equation :—

$$SiF_4 + 3H_2O = SiO(OH)_2 + 4HF.$$

or,

$$SiF_4 + 4H_2O = Si(OH)_4 + 4HF.$$

The silicic acid separates as a gelatinous mass, and the hydrofluoric acid unites at once with another portion of silicon fluoride, forming fluosilicic acid, which remains in solution and can afterwards be separated by filtration. The whole reaction may, therefore, be thus represented :—

$$3SiF_4 + 3H_2O = SiO(OH)_2 + 2H_2SiF_6,$$

or,

$$3SiF_4 + 4H_2O = Si(OH)_4 + 2H_2SiF_6.$$

The glass tube leading the silicon fluoride into the water, even when wide, becomes easily stopped up by the deposited silicic acid, and so an explosion might be produced. In order to avoid such an occurrence a little mercury is placed at the bottom of the vessel in which the fluosilicic acid is to be produced. The tube from the flask evolving the silicon fluoride is made to dip under this mercury,

and the vessel then filled up with water. The decomposition of the silicon fluoride then only commences above the level of the mercury. The danger of an explosion may also be avoided by connecting the end of the delivery tube with the neck of a glass funnel, and dipping the large open end in the water, so that the gas comes at once into contact with a large surface of water.

The aqueous fluosilicic acid, when separated from the silicic acid by filtration, is a strongly acid colourless liquid. It may be concentrated up to a certain point by evaporation at the ordinary temperature of the air. But if this limit is exceeded, or if the liquid is heated, it decomposes into silicon fluoride and hydrofluoric acid, both of which volatilize. On heating, therefore, a solution of fluosilicic acid in a platinum basin, ultimately nothing remains.

By neutralizing fluosilicic acid with bases or carbonates, its salts—the fluosilicates—are obtained, having the general composition: R'_2SiF_6, where R′ is one atom of a monad metal. These salts are mostly soluble in water except the barium compound: $BaSiF_6$, and those of potassium and sodium. As the strontium salt is easily soluble in water, fluosilicic acid has been used as a means of separating barium and strontium.

In concluding this account of the compounds of silicon, brief reference may be made to certain substances which are of interest on account of analogy with similar compounds of carbon usually included under the head of organic chemistry (compare p. 268). In lack of suitable names for these compounds they are usually called after the corresponding carbon compounds; thus the body corresponding to chloroform ($CHCl_3$) is called silico-chloroform.

Silico-chloroform: $SiHCl_3$, is produced when amorphous silicon is heated in a stream of dry hydrochloric acid gas. At the same time a small quantity of the less volatile tetrachloride is also produced, which can be separated by fractional distillation. This compound is a colourless inflammable liquid, fuming in the air, with a specific gravity of 1·65 and boiling at 36°. Chlorine converts it into silicon tetrachloride and hydrochloric acid, and water, even at 0°, into hydrochloric acid and a compound of the composition: $Si_2H_2O_3$, corresponding to the hypothetical formic anhydride: $\left.\begin{matrix}HCO\\HCO\end{matrix}\right\}O$.

Silico-formic Anhydride: $\left.\begin{matrix}HSiO\\HSiO\end{matrix}\right\}O$, produced as just mentioned, is a white powder, which when heated in the air burns easily to silica and water. Caustic soda easily dissolves it, with evolution of hydrogen, forming sodium silicate.

Silicoxalic Acid: $\left\{\begin{matrix}SiO\cdot OH\\SiO\cdot OH\end{matrix}\right.$ is obtained as a white powder by decomposing silicon hexachloride with water, and is dissolved by caustic soda to form sodium silicate. In composition it corresponds to the carbon compound, oxalic acid: $\left\{\begin{matrix}CO\cdot OH\\CO\cdot OH\end{matrix}\right.$ with which, however, it has no other similarity; it does not even possess the properties of an acid.

CARBON.

Chemical Symbol: C.—*Atomic Weight*: 12.

Carbon occupies a peculiar position among the other elements. Although it only combines directly with few other elements—with oxygen, sulphur, hydrogen, and iron, but neither with nitrogen nor the halogens—the compounds of carbon far exceed those of any other element both in number and variety. All organic compounds, including the constituents and products of all animal and vegetable organisms, as well as the numerous substances which can be artificially prepared from them, are compounds of carbon.

Organic chemistry has been defined as the chemistry of the carbon compounds, according to which a description of these substances should find no place in a text-book of inorganic chemistry. But sharp lines of demarcation, which so completely separate substances from one another as to make a strict classification possible, are unknown in nature. Connecting links are everywhere to be found showing a gradual transition from one class of substances to the other. And although all organic compounds contain carbon, this by no means compels us to refer all carbon compounds to organic chemistry; many of the carbon compounds, especially those of simpler composition, cannot be easily separated from the inorganic compounds of other elements.

Carbon occurs free in nature in three modifications, as different

from one another in their physical properties as could be imagined. We know it, firstly, as the diamond, crystalline, transparent, characterized by its great hardness and high index of refraction for light, and a non-conductor of electricity; secondly, as graphite, with a dark grey colour, crystalline, lustrous, a conductor of electricity, and extremely soft; and, lastly, as charcoal, the chief constituent of common coal, amorphous, black, not much harder than graphite, and a non-conductor of electricity.

The diamond is among the rarest of substances and is the most precious of gems; graphite is found in large quantities, but usually in isolated spots; amorphous carbon, as the various forms of coal, occurs widely distributed and in immense quantities. The last-named variety, although by far the cheapest, is still by far the most valuable and important. It furnishes the most important source of our artificial heat, light, and power, and influences not only the industrial, but also the entire social and political life of the civilized countries in which it occurs.

Like their other physical properties, the specific gravity of the three modifications of carbon is very different. That of the diamond is 3·5, of graphite 2·2, and of amorphous carbon 1·6 to 2·0.

Greater similarity, however, exists between the chemical properties of the three forms. Although they burn in oxygen or air with different degrees of readiness, they all produce the same products of combustion. Equal weights of either modification always produce equal weights of carbonic acid. And by the reduction of carbonic acid, carbon is again formed, but only amorphous carbon or graphite, never diamond. All attempts to prepare the diamond by the reduction of carbonic acid or by any other method have, as yet, been unsuccessful.

Carbon in all three forms is infusible at all temperatures, but volatilizes at the high temperature of the electric arc; it is insoluble in any of our ordinary solvents. The only solvent at present known is fused iron, which, however, only dissolves 1 or 2 per cent. of it. On cooling, most of the carbon separates out in the form of graphite. Should a liquid ever be discovered capable of dissolving carbon at not too high a temperature, the carbon might be again separated in the diamond form. (See Appendix.)

As was stated above, carbon does not unite directly with nitrogen nor with the halogens, and carbon compounds of these substances can only be obtained indirectly. Even with oxygen,

sulphur, and hydrogen, carbon has not the slightest tendency to combine, either at the ordinary temperature or at 100°. But when heated to redness its affinity for oxygen and sulphur gradually increases, so that at a white heat the affinity of carbon for oxygen and sulphur even surpasses that of phosphorus and potassium. Carbon when heated to redness is, therefore, one of the most powerfully reducing substances known, and a very extended use is made of this property in the extraction of metals from their ores.

Hydrogen only unites with carbon at the extremely high temperature of the electric arc. When this is produced between carbon poles in an atmosphere of hydrogen, small quantities of a compound of the two bodies, called acetylene: C_2H_2, are produced.

Under certain circumstances carbon can also unite directly with nitrogen when a substance—*e.g.* potassium—is present with which the compound of the two elements (cyanogen) can combine. From carbon, nitrogen, and potassium carbonate we can thus obtain potassium cyanide.

The *diamond* is always found in alluvial deposits, which have been produced by the disintegration of older rock masses, and from which it is obtained by a process of washing. *Diamond-fields*, or districts which yield diamonds, occur especially in Brazil, India, and at the Cape, as well as in California, Borneo, and in the Ural Mountains. Diamonds have also been found in Brazil in a matrix of a variety of talc schist rich in quartz—termed *itacolumite*, and distinguished by the ease with which thin strips of it may be bent. But whether this is the original matrix of the diamond, or whether the itacolumite was built up from older rock with the diamonds, remains as yet undecided.

The diamond crystallizes in the regular system, and its faces are often curved. The crystals may be readily fractured parallel to the faces of the octahedron; it is distinguished by its great hardness and bright lustre. Diamonds are usually transparent and colourless, or faintly yellow. They are sometimes found of a bright yellow or brown colour, and sometimes even blue, green, and black.

Diamonds used as jewels always require cutting and polishing, which, on account of their great hardness, can only be done with diamond dust. Small diamonds useless for other purposes—

diamond-boart—are crushed in a steel mortar. Notwithstanding the great hardness of the diamond, it is tolerably brittle, and can therefore be easily reduced to powder.

The form which the diamond receives when ground for a gem depends partly upon its original form, and partly upon the use to which it is to be put. The most valuable form is that known as the *brilliant* (fig. 52), which may be described as two cones placed base to base, of which the upper one is cut off at about half its height. Both pyramids are made up of a number of triangular or oblong

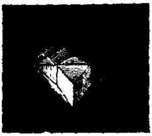


Fig. 52.

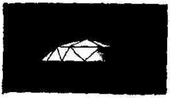


Fig. 53.

faces (facets). The brilliant form is always held by its centre parts in the setting, so that both upper and lower pyramids are free. Differing from this is the *table* or *rosette* form (fig. 53), consisting of a flat base, on which rises a circle of oblong facets, supporting a hexagonal pyramid.

The value of a diamond depends partly on its size, partly on its transparency (water), and partly on its play of colours. The weight of a diamond is expressed in carats (0·205 gramme, or 3·165 grains), but the value of a diamond, other things being equal, is not proportional to its weight, but to the square of its weight. Thus, if one diamond weighs ten times as much as another, its value will be approximately a hundred times as much.

Large diamonds of 100 to 300 carats (20·5 to 61·5 grammes) are very rare, and are mostly crown jewels. To these belong the so-called Star of the South, found in Brazil, and weighing 127 carats, and the Koh-i-Noor, of 106 carats, found in India, and one of the English crown jewels. Of the two largest diamonds known, one weighs 194 carats, is of a yellowish colour, and is fixed at the end of the Russian sceptre; the other, weighing 277 carats, is in the possession of the Nizam of Hyderabad.

Of the formation of the diamond nothing for certain is known, except that it is not produced at a high temperature. Its optical

properties and microscopical observations seem to show that the diamond is of organic origin. All attempts to prepare diamonds artificially have as yet given no certain result, although it is always more probable that a method might be discovered for converting amorphous carbon or graphite into diamond, or of preparing the diamond in some other way, than that the problem of the alchemists—the transmutation of common metals into gold—should ever be solved.

The present high price of diamonds is due to their scarcity. Should larger quantities of diamonds ever be discovered, or should it ever be possible to prepare them artificially, their value would be considerably diminished.

On account of its hardness, the diamond is largely used for cutting hard stones, and for scratching and cutting glass. For simply writing on glass, a splinter of diamond is sufficient, but if the glass is to be cut, a deeper scratch is required, and a natural convex edge of the diamond is necessary.

The diamond requires a higher temperature for its combustion than amorphous carbon, but burns easily in the oxy-hydrogen blowpipe with excess of oxygen, or when raised to redness by a spiral of platinum wire connected with a galvanic battery in an atmosphere of oxygen. In the finely divided state the diamond burns readily in the air when heated on a piece of platinum foil before the blowpipe. In absence of oxygen, for example, in an atmosphere of hydrogen, the diamond may be heated to a high temperature without any appreciable change.

Graphite, *plumbago*, or *blacklead*, occurs in nature in nodular or columnar masses, and occasionally in small tablets belonging to the hexagonal system. It is of a dark grey colour, opaque, a good conductor of electricity, feels greasy to the touch, and is so soft that it easily marks paper. Its specific gravity varies from 2·5 to 1·8, according as it is more or less pure. Graphite usually occurs in isolated spots, but often in considerable quantities. The mines of Cumberland and Westmoreland are the oldest, but are now nearly exhausted. It is also found in Passau and other parts of Germany and Austria, in Bohemia, Greenland, Sicily, and Ceylon, and, in large quantities of great purity, in California. Graphite may be artificially prepared by solution of carbon in molten iron, when it partly separates out on cooling.

Finely powdered and pure graphite can be easily compressed

at a high temperature to a compact mass of the same specific gravity as that occurring in nature. It is only necessary to remove air as much as possible by an air-pump before compressing. Thin plates or threads for black-lead pencils can be easily sawn from the blocks obtained by this process.

Compact graphite burns almost as difficultly and sometimes more difficultly than the diamond.

If finely powdered graphite is mixed with three times its weight of powdered potassium chlorate, and with enough concentrated nitric acid to make a thin paste, then heated for several days to 60°, or placed in direct sunlight until yellow vapours are no longer given off, it becomes changed to a bright yellow, transparent, crystalline substance of the composition : $C_{11}H_4O_5$. By repeating the process several times the whole may be changed into this substance. It is slightly soluble in water and possesses a faint acid reaction, dissolves readily in aqueous alkalies, and in general has all the properties of an acid. This peculiar acid is called *graphitic acid.*

The graphite which occurs in nature is never pure, but contains smaller or larger quantities of inorganic constituents, which remain behind as ash on burning.

Graphite is of considerable value in the arts. It is used for the manufacture of black-lead pencils, and of crucibles which are to withstand a high temperature, and which are made of a mixture of powdered graphite and clay. It is further employed for polishing the grains of gunpowder, for coating moulds of gutta-percha or plaster to make them conductors of electricity in the process of electrotyping, and finally for blacking iron grates and other articles of the same metal, which by receiving a coating of the material are protected to some extent from rusting.

Amorphous carbon is produced from organic substances when they are heated to redness, or when they decay out of contact with the air. Wood charcoal may be chosen as representative of amorphous carbon which has been produced by the first-named process. As its name implies, this substance is obtained by charring wood out of contact with the air, and is prepared either by piling logs of wood together, covering with sods, and then slowly burning them, or else by heating wood or sawdust in iron retorts. By the first process only charcoal is obtained ; but by the second and more modern, various volatile products of considerable value,

such as acetic acid (pyroligneous acid), wood naphtha, creosote, &c., are obtained. According to the kind of wood used the charcoal may be more or less porous, and therefore of apparently different specific gravity.

The different varieties of wood charcoal are employed for different purposes; large quantities are used for the manufacture of gunpowder. Charcoal is also used (largely in some countries) as a fuel. When heated to redness in the air, it burns without smoke or flame, and produces a considerably higher temperature than the same weight of wood. Wood charcoal is extremely porous, and possesses the property of absorbing considerable quantities of atmospheric air. Gases which are more easily liquefied than common air—for example, ammonia, sulphuretted hydrogen, sulphurous anhydride, and carbonic acid—are absorbed by charcoal in even greater quantities. It thus possesses the power of absorbing noxious gases from the air, and purifies or disinfects the air. Organic substances which may be suspended or dissolved in drinking water and impart a disagreeable taste or smell are removed when such water is shaken up with charcoal, or when the water is passed through a filter of powdered charcoal. The water which runs through such a filter is usually clear, odourless, and pleasant to the taste, and charcoal filters are therefore often employed to purify drinking water. Colouring matter of various kinds is easily removed from a liquid by amorphous charcoal—claret, for example, is easily decolorized. This property is possessed in a much higher degree by the charcoal obtained from animal substances—called animal charcoal—than by wood charcoal.

Animal Charcoal—known also as bone-black, animal-black, ivory-black, &c.—is obtained by glowing blood, bones, and other animal refuse, excluded from the air. It contains all the inorganic substances—principally calcium phosphate and carbonate—present in the substances from which it was prepared. These two compounds can be readily extracted by warming the charcoal with hydrochloric acid, when, after washing with water, a form of amorphous carbon remains, which far exceeds wood charcoal in porosity and absorption power. Animal charcoal purified in this way is largely used for many technical purposes, especially to decolorize the syrup in sugar refineries. Barium and strontium hydrates have almost displaced animal charcoal in the purification of sugar (p. 409).

Wood charcoal contains less inorganic impurity than animal

charcoal, but is still far from being pure carbon. When burnt in the air it leaves behind a considerable ash, rich in potassium carbonate. Pure amorphous carbon may be obtained by glowing certain organic substances free from nitrogen and inorganic impurities. Pure crystallized sugar or tartaric acid, for example, when glowed in a platinum basin and afterwards heated strongly in a covered platinum crucible, yields a very pure form of amorphous carbon. *Gas-black* is the purest form of amorphous carbon.

Impure amorphous carbon is found in nature as the various forms of *coal* which have been produced by the decay of vegetable matter out of contact with the air, and sometimes also by elevation in temperature and strong pressure. All varieties contain, besides inorganic constituents—their ash which they leave behind on burning—varying quantities of hydrogen, oxygen, nitrogen, and sulphur, which are mostly driven off when the coal is heated in closed vessels. The heavy form of carbon produced by charring coal in closed vessels is called *coke*. Coke is an excellent fuel, and produces, when freely supplied with air, a higher temperature than ordinary coal. It is very largely used for smelting iron and other ores. Coke is of a dark grey colour, lustrous, and a conductor of electricity, and is therefore a variety of graphite.

The different varieties of coal may be classified according as the charring process which they have undergone has been more or less complete—*i.e.* according to their relative proportions of carbon, hydrogen, and of oxygen and nitrogen. Coal is usually black in colour, mostly of slaty fracture and fatty lustre, and when heated in the air generally evolves combustible gases, and therefore burns with a flame.

Anthracite is the most highly carbonized form of coal. It is distinguished by its hardness and conchoidal or shell-like fracture; it produces very little gas when heated, and therefore burns almost without flame. Anthracite is found in considerable quantities in South Wales and in Pennsylvania, and is highly valued as a smokeless steam-coal and for metallurgical purposes. It does not soil the fingers like common coal.

Bituminous coal in its varied forms comes next to anthracite in percentage of carbon. All the commoner kinds of coal belong to this class. It contains varying proportions of carbon and hydrogen, but always more hydrogen and less carbon than anthracite. Bituminous coals rich in hydrogen evolve considerable quantities of gas when heated, and are therefore used for the manufacture of

coal-gas. A variety rich in volatile matter, and especially suited for gas making, is *cannel coal*. This is much more compact in structure than ordinary bituminous coal, and, like anthracite, has a conchoidal fracture, but its surface is dull, not bright and lustrous like common coal and anthracite.

Brown coal or *lignite* is always of more recent formation than ordinary coal. It is mostly soft and of a brown colour, and often exhibits distinct traces of woody structure not to be found in the older coals. It contains considerably more hydrogen, oxygen, and nitrogen than ordinary coal and less carbon.

Jet is a compact, black form of lignite, hard enough to take a high polish, and largely used for ornamental articles.

Peat or *turf* is produced in marshy localities by the gradual decay of grasses, mosses, and other marsh plants. It contains large quantities of inorganic constituents, and leaves a large amount of ash when burnt. It is of much less value as a fuel than any of the varieties of coal mentioned above.

The following table[1] gives the approximate percentage composition of the organic parts of wood, peat, and the different kinds of coal, omitting the ash in all cases :—

	Carbon	Hydrogen	Oxygen, Nitrogen, and Sulphur
Oak	50·17	6·08	43·75
Peat	59·83	5·78	34·39
Lignite (Bovey Tracey) . .	67·90	5·73	26·37
Staffordshire coal . . .	79·37	5·37	15·26
Wigan cannel coal . . .	82·47	5·67	11·86
Newcastle caking coal . .	87·95	5·34	6·71
South Wales anthracite . .	91·85	3·35	4·80

Amorphous carbon in a finely divided state is obtained as *soot*, *lampblack*, or *gas-black* by the incomplete combustion of volatile organic compounds, rich in carbon, such as turpentine, benzol, or wood containing turpentine and resin. If a cold body is placed in the flame of a candle or oil-lamp it soon becomes covered with soot or finely divided carbon, just as arsenic is deposited from the flame of burning arsine. Lampblack is used in a more or less pure state for various purposes—the finer varieties for preparing Indian ink, the more coarse as a black paint and for printer's ink. Unless purified by special processes, it always contains varying quantities of hydrocarbons mixed with it.

[1] From Watts's *Dictionary of Chemistry*.—ED.

COMPOUNDS OF CARBON.

No element exists in so large a number of compounds as carbon. By far the largest proportion of these belongs to organic chemistry, and we should be justified in referring all compounds of carbon to this division, if it were possible to separate inorganic and organic compounds distinctly from one another, and if it were not absolutely indispensable to describe some of the more simple of the carbon compounds under inorganic chemistry.

To these belong carbonic acid and oxide, oxalic acid, carbon disulphide and oxysulphide, carbon tetrachloride, marsh gas and cyanogen, together with hydrocyanic acid, the cyanides, and a few other compounds.

CARBONIC ANHYDRIDE, or CARBONIC ACID.[1]

Composition: CO_2.

Carbonic acid, which is always produced when carbon in any form or any compound of carbon is burnt with a free supply of air, is a colourless gas, of peculiar prickly smell and faintly acid taste.

It occurs very widely distributed in nature, both free and combined with various bases. It is a normal constituent of atmospheric air (p. 200), and is contained in most natural waters in the free state. In immense quantities combined with lime it forms the different natural varieties of calcium carbonate—common *limestone*, *calcspar*, *arragonite*, *marble*, *chalk*, &c.; further, as magnesium carbonate in *magnesite*, as double carbonate of calcium and magnesium in *dolomite*, as ferrous carbonate in *spathic iron ore*, as barium and strontium carbonates in *witherite* and *strontianite* respectively, and, finally, as sodium carbonate in *trona* or *soda*—to mention only the more important compounds.

In many places, carbonic acid is evolved in considerable quantities from clefts in the earth, usually in the neighbourhood of active or extinct volcanoes. The gas is, of course, invisible, but can be easily recognized by chemical means. Among the most

[1] True carbonic acid, which would result from the union of the anhydride with water, is unknown, and the anhydride (CO_2) is therefore usually called carbonic acid, for the sake of brevity.—ED.

celebrated localities of these carbonic acid springs are the Grotto del Cane, near Naples, those in Pyrmont, and in various parts of Germany, and the well-known poison valley of Java. Generally, the carbonic acid carries water with it in its upward course to the surface of the earth, and often with considerable force, owing to the pressure of the gas. At Nauheim a spring rises 80 feet high, probably owing to the force with which the compressed carbonic acid escapes.

Finally, carbonic acid is produced in such large quantities during the fermentation of sugar in the manufacture of alcoholic liquors, that attempts have been made to utilize the gas—for example, in the manufacture of white-lead.

It is thus clear that there is no lack of material from which carbonic acid may be prepared; but if the gas is wanted pure, the choice of substances becomes more limited. All limestones which contain traces of organic matter when treated with strong acids yield carbonic acid with an unpleasant odour and taste, because small quantities of these organic substances are carried away with the gas. And carbonic acid prepared from such material should therefore never be used for the manufacture of mineral waters. On the other hand, the gas evolved from calc-spar, marble, magnesite, and many kinds of dolomite and limestone, as well as from acid sodium carbonate, is always pure and free from any foreign smell or taste.

For the preparation of small quantities of carbonic acid *Kipp's* apparatus is best adapted, especially as with this arrangement a stream of pure carbonic acid can be obtained at any time by simply opening a stop-cock. Carbonic acid may be evolved from magnesite or acid sodium carbonate by means of dilute sulphuric acid, and need then only be dried (when necessary) by passing through concentrated sulphuric acid. To prepare carbonic acid from dolomite or calcium carbonate, it is better to use hydrochloric acid, as sulphuric acid produces difficultly soluble calcium sulphate, which surrounds the pieces of marble or dolomite and tends to prevent their contact with the acid. If sulphuric acid is preferred, the limestone or dolomite must be finely powdered, and the mixture continuously agitated. The process is represented by the following equation:—

$$CO \cdot O_2Ca + SO_2(OH)_2 = SO_2 \cdot O_2Ca + H_2O + CO_2$$

When carbonic acid is liberated from limestone or marble with dilute hydrochloric acid, calcium chloride then remains behind in solution, and the equation becomes:—

$$CO \cdot O_2Ca + 2HCl = CaCl_2 + H_2O + CO_2$$

The gas prepared in this way carries some of the volatile acid with it, and should be freed from this by passing through several wash-bottles filled with water.

Carbonic acid may be collected over mercury or over water, in which it is only slightly soluble. At the ordinary temperature water dissolves about its own volume of the gas. Since, however, carbonic acid is considerably heavier than air, vessels are best filled with the gas, especially when required dry, by leading the gas with a long glass tube to the bottom of the vessel to be filled (fig. 54). The carbonic acid then gradually displaces the lighter air until in a short time the whole vessel is filled with the gas.

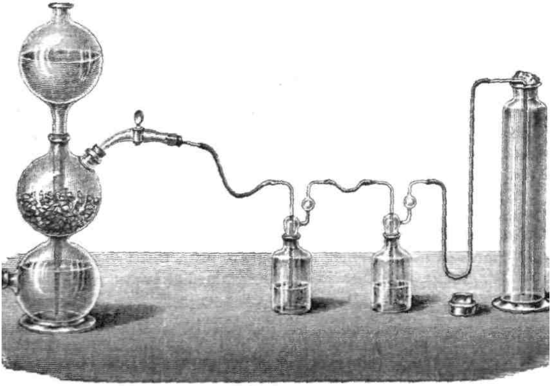


Fig. 54.

Carbonic acid has a specific gravity of 1·52, corresponding to a molecular weight of $1{\cdot}52 \times 28{\cdot}88 = 44$, and its molecule is therefore CO_2. It is thus considerably heavier than air, and diffuses from an open jar so slowly that it can be poured like water from one vessel to another. If two jars are taken, one filled with carbonic acid and the other with air, the carbonic acid can, with care, be poured almost completely from one into the other as may be easily shown by introducing a burning taper.

Carbonic acid neither burns nor supports combustion. A burning candle is at once extinguished in a jar of the gas; even if

the air only contains a small quantity of carbonic acid, a candle ceases to burn. Respiration in such an atmosphere is also impossible, and carbonic acid, without being actually poisonous, is fatal to the life of animals, because it takes the place of the oxygen necessary to aërate the blood. Death therefore ensues simply from suffocation. That carbonic acid is not a true poison is at once evident from the following considerations: we continuously inhale carbonic acid, largely diluted it is true, into our lungs; carbonic acid is continually produced in considerable quantities by the slow combustion going on in our bodies, and forms a large proportion of the air exhaled from our lungs; finally, continued use of effervescing drinks, rich in carbonic acid, does not apparently produce any injurious effect.

Nitrogen, like carbonic acid, neither burns nor supports combustion, nor can it be respired; the latter gas may, however, be distinguished from the former by the fact that when brought into contact with clear lime-water it at once produces a white turbidity or precipitate of calcium carbonate, insoluble in water, but which again dissolves with effervescence in dilute hydrochloric acid. Baryta-water is even better adapted than lime-water for the detection of carbonic acid.

Carbonic acid possesses the properties of a weak acid anhydride, and unites therefore with bases. The combination, however, takes place slowly, and but little heat is evolved. If a glass tube closed at one end is filled with carbonic acid and the open end placed in a vessel of caustic potash, the liquid rises in the tube slowly, more quickly if shaken, until ultimately the whole of the carbonic acid disappears. We employ this property of the gas not only to separate it when mixed with other indifferent gases, but also to determine its amount quantitatively.

The quantity of carbon present in an organic substance is found by heating it with some substance that readily gives up oxygen (*e.g.* copper oxide) in a tube of hard glass. By this process the hydrogen present is converted into water, and the carbon into carbonic acid. These compounds are allowed to pass first through a U-tube containing calcium chloride, or, better, concentrated sulphuric acid to absorb the water, and then through a series of bulbs (called Liebig's potash-bulbs, fig. 55), which contain strong caustic potash, and absorb the carbonic acid. If the calcium chloride tube and the potash bulbs are separately weighed before and after the experiment, the increase in weight of the former gives the weight

of water formed, and of the latter the weight of carbonic acid. From these weights the actual weights of hydrogen and carbon present in the substance can be easily calculated.

The affinity of carbon for oxygen increases as the temperature rises, and at a white heat carbon can even extract oxygen from potassium oxide or carbonate and set free metallic potassium. But at a red-heat, and when the carbonic acid is in excess, potassium can abstract oxygen from carbonic acid. If a small piece of potassium is heated in a bulb-tube of hard glass to low redness while a stream of dry carbonic acid is passed over it, the fused metal soon begins to burn with a dark red light, and becomes covered with a coating of potassium carbonate and amorphous carbon. The following equation explains the process :—

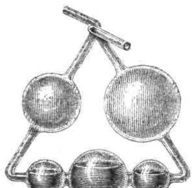


Fig. 55.

$$4K + 3CO_2 = 2CO(OK)_2 + C.$$

This experiment shows that colourless carbonic acid contains black charcoal, and that it can be reduced to this substance.

Carbonic acid is the anhydride of an unknown dibasic acid, the composition of which would be : $CO\begin{cases}OH\\OH\end{cases}$ but which has not yet been prepared. The majority of its salts are insoluble in water ; the only soluble carbonates being those of the alkali metals : potassium, sodium, lithium (ammonium, rubidium, and cæsium), and of thallium. Normal potassium carbonate (potashes) and normal sodium carbonate (soda) possess an alkaline reaction, because the strong basic properties of these oxides are not completely neutralised by the weak carbonic acid. Its acid salts of these two metals—*e.g.* acid sodium carbonate : $CO\begin{cases}OH\\ONa\end{cases}$—react neutral.

When carbonic acid is led into aqueous ammonia the chief product is ammonium carbonate, of the composition : $CO\begin{cases}ONH_4\\ONH_4\end{cases}$:—

$$CO_2 + 2NH_3 + H_2O = CO\begin{cases}ONH_4\\ONH_4\end{cases}$$

This salt cannot, however, be produced from dry ammonia and dry carbonic acid, because the molecule of water necessary

for its production is now absent. The two gases unite, however, with considerable evolution of heat, and produce a salt, which is ammonium carbamate, having the composition: $CO\left\{\begin{matrix}NH_2\\ONH_4\end{matrix}\right.$ (p. 186).

Carbonic acid can be condensed by a high pressure to a liquid which, when allowed to evaporate in the air, produces a sufficient diminution in temperature to freeze it. For the preparation of liquid carbonic acid, the apparatus devised by Natterer was formerly universally employed, but has now been completely abandoned. It consisted of a compression pump, worked by hand, and a wrought-iron vessel. The latter vessel (fig. 56) is screwed at its base to the top of the cylinder of the pump, and is there provided with a small valve opening upwards at the end of every stroke of the piston, and otherwise kept closed by a weak spiral spring. This valve, therefore, only allows gas to enter the strong vessel, and prevents any from leaving it. For many years past, liquid carbonic acid has been prepared on a large scale by pumps worked by steam, which condense the carbonic acid and pump it into steel cylinders. These cylinders are provided with two valves, one which just goes inside the cylinder to deliver the gas, and another going nearly to the bottom of the cylinder for delivery of the liquid. In this form liquid carbonic acid is sent into trade in large quantities.

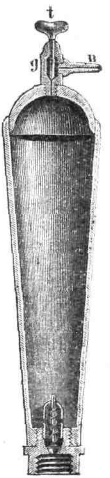


Fig. 56.

If a jet of liquid carbonic acid is allowed to flow out of the side tube into a metallic vessel, which is so arranged that it receives a circular motion, and therefore rapidly evaporates, a large portion of the carbonic acid freezes at the low temperature produced, and fills the vessel as a light, snow-like mass.

Condensed carbonic acid is a colourless, transparent, mobile liquid of 0·95 specific gravity at 0°, and only 0·78 at + 25°. It therefore expands under the influence of heat not only greater than any other liquid, but also greater than the gases—a very remarkable property.

The tension of liquid carbonic acid at different temperatures is about as follows :—

At $-79°$	. . . . .	1·1 atmospheres.
„ $-30°$	. . . . .	18 „
„ $-10°$	. . . . .	27 „
„ $0°$	. . . . .	36 „
„ $+10°$	. . . . .	46 „
„ $+30°$	. . . . .	74 „
„ $+35°$	. . . . .	80 „

During free evaporation in the air its temperature falls to about $-79°$.

The solid, snow-like carbonic acid evaporates but slowly even on a warm hand, and notwithstanding its low temperature produces scarcely a feeling of cold. It does not, in fact, touch the hand at all, but is separated by a layer of the gas which it is continually giving off. The phenomenon is similar to that produced when a drop of cold water is allowed to fall into a red-hot platinum dish; the drop then remains suspended by its own vapour and does not touch the hot metal at all. If, however, a piece of solid carbonic acid is pressed firmly on the skin, a burning pain is felt and a blister is raised on the spot touched. The action is, in fact, the same as when the skin is burnt with a hot body.

If solid carbonic acid is mixed with some volatile liquid—*e.g.* ether—both evaporate with great rapidity, the mixture begins to boil, and a sufficiently low temperature (about $-100°$) is produced to freeze mercury in a few seconds.

Carbonic acid is largely used for the manufacture of artificial mineral waters. Pure water in which various salts are dissolved, according to the mineral water required, is impregnated with carbonic acid in thick metallic vessels. The gas is pumped in by a special apparatus, and the liquid is kept constantly agitated. In this way not only can many mineral waters be imitated, but other compositions of any required kind can be prepared. Water in which small quantities of salts have been dissolved retains its carbonic acid when exposed to the air longer than pure water.

Carbonic acid is also used in the arts for the preparation of white-lead, and of salicylic acid from phenol. Liquid carbonic acid is now employed on a large scale by Krupp at Essen, in Germany, for compressing cast-steel during solidification.

CARBAMIC ACID.

Composition of the hypothetical acid: $CO\left\{\begin{matrix}NH_2\\OH\end{matrix}\right.$

As previously mentioned (p. 290), dry carbonic acid and dry ammonia unite to form a salt which cannot be ammonium carbonate, as the molecule of water necessary for the formation is wanting.

The compound produced is the ammonium salt of a monobasic acid, which is as little known in the free state as the true carbonic acid: $CO\left\{\begin{matrix}OH\\OH\end{matrix}\right.$. It has the same relation to this dibasic acid as chlorsulphonic acid (p. 165): $SO_2\left\{\begin{matrix}Cl\\OH\end{matrix}\right.$ has to sulphuric acid, except that carbamic acid contains an atom of amidogen, instead of one of chlorine, in place of an atom of hydroxyl. (See footnote, p. 311.)

The production of ammonium carbamate may be easily understood if we imagine one of the two molecules of ammonia, which unite with one molecule of carbonic acid, to give up an atom of hydrogen to the other. By this means amidogen is produced on the one hand, and ammonium on the other, which then unite with the carbonic acid as shown by the following equation:—

$$CO_2 + 2NH_3 = CO\left\{\begin{matrix}NH_2\\ONH_4\end{matrix}\right.$$

Ammonium carbamate is easily obtained by leading carbonic acid and ammonia, both perfectly dry, into absolute alcohol, when the salt separates as a white, voluminous, crystalline mass. When heated with absolute alcohol in sealed tubes to 100° and allowed to cool slowly, the salt separates out in large thin crystalline plates.

This salt is always contained together with ammonium carbonate in the commercial carbonate of ammonia. In contact with water it gradually takes up a molecule of this substance, and after some time is converted into ammonium carbonate. It is distinguished from this latter compound by the fact that its aqueous solution when mixed with a solution of calcium chloride does not at once deposit a white precipitate of calcium carbonate, because the calcium carbamate which is first produced is soluble in water.

Calcium carbamate: $(CONH_2)_2O_2Ca + H_2O$, is produced when

carbonic acid is led into a mixture of thick milk of lime and four times its volume of strong ammonia. The filtered liquid is then cooled to 0° and precipitated with absolute alcohol: the amorphous precipitate thus produced soon changes into small prismatic crystals of the above composition. Calcium carbamate is tolerably soluble in water, but the solution soon becomes turbid from the calcium carbonate produced by its decomposition with water. In aqueous ammonia the salt remains longer undecomposed. When gently heated it loses its water of crystallization, and then bears a temperature of 180° without decomposition.

The *urethanes* are a series of stable organic compounds which carbamic acid forms with the alcoholic radicals.

Ammonium carbamate, which contains the constituents of one molecule of water less than ammonium carbonate, contains itself one molecule of water more than carbamide, thus:—

Ammonium carbonate . . . . . $CO\begin{cases}ONH_4\\ONH_4\end{cases}$

Ammonium carbamate . . . . . $CO\begin{cases}ONH_4\\NH_2\end{cases}$

Carbamide or urea . . . . . $CO\begin{cases}NH_2\\NH_2\end{cases}$

Carbamide or urea is a normal constituent of urine; it may be considered either as the hypothetical carbonic acid in which both atoms of hydroxyl have been displaced by amidogen, or as carbonic anhydride in which one atom of oxygen is displaced by two of amidogen. Ammonium carbonate and also ammonium carbamate are converted with loss of water into urea, when heated in sealed tubes up to 140°.

CARBONIC OXIDE OR CARBON MONOXIDE.

Composition: CO.

The second lower oxide of carbon, which contains the element as a diad, is, like carbonic acid, a colourless gas, but is distinguished from this compound principally by its combustibility. When heated in the air it catches fire and burns with a blue flame, forming carbonic acid.

Carbonic oxide has a specific gravity of 0·968, corresponding to

a molecular weight of 28, is scarcely soluble in water, and is only condensed to a liquid under the greatest pressure at a very low temperature. (See Appendix.) The gas, although tasteless and odourless, is very poisonous; air containing only a few per cent. of it when breathed produces giddiness and intense headache, followed by insensibility, and after a little time by death.

Carbonic oxide does not occur free in nature like carbonic acid, but is always produced by the incomplete combustion of carbon or carbonaceous substances—*i.e.* when these are burnt with an insufficient supply of air. It may also be prepared from carbonic acid if this gas is led over glowing charcoal. The blue flames seen when air flows freely over large masses of glowing carbon—for example, when the door of the firebox of a steam-engine is opened—are due to burning carbonic oxide, produced by the contact of carbonic acid with the red-hot carbon.

For the preparation of carbonic oxide it is best to employ either *oxalic or formic acid, or else a salt of the last-named acid.*

Oxalic acid, which occurs in nature in many plants, especially the sorrels, and which can also easily be prepared artificially, is a solid crystalline substance of strong acid properties, and having the composition $\left\{\begin{matrix} CO\cdot OH \\ CO\cdot OH \end{matrix}\right.$. This body, when mixed with concentrated sulphuric acid and warmed, breaks up into water, carbonic acid, and carbonic oxide:—

$$\left\{\begin{matrix} CO\cdot OH \\ CO\cdot OH \end{matrix}\right. = H_2O + CO_2 + CO.$$

The sulphuric acid first removes the water of crystallization from the oxalic acid, and then, on account of its strong attraction for water, abstracts a further two atoms of hydrogen and one of oxygen, which unite to form water. As, however, the oxalic anhydride: $\left.\begin{matrix} CO \\ CO \end{matrix}\right\} O$, which is thus produced, does not appear to exist, this hypothetical substance at once breaks up into carbonic acid and carbonic oxide:—

$$\left.\begin{matrix} CO \\ CO \end{matrix}\right\} O = CO_2 + CO.$$

In order to purify the carbonic oxide from the large quantities of carbonic acid mixed with it, the mixed gases must be passed through a system of wash-bottles containing strong caustic potash, which absorbs the carbonic acid, but allows the carbonic oxide to

pass on unchanged. If the gases are evolved rapidly, it is difficult to separate the whole of the carbonic acid from the mixture. It is, therefore, better to prepare the carbonic oxide from formic acid, which breaks up when heated with sulphuric acid into carbonic oxide and water only.

Formic acid is a monobasic acid of the composition : $\begin{cases} H \\ CO \cdot OH, \end{cases}$ and its sodium salt is : $\begin{cases} H \\ CO \cdot ONa \end{cases}$. On heating this compound with concentrated sulphuric acid, formic acid is first set free, and this is then decomposed into carbonic oxide and water. The following equation expresses the entire reaction :—

$$\begin{cases} H \\ CO \cdot ONa \end{cases} + SO_2 \begin{cases} OH \\ OH \end{cases} = SO_2 \begin{cases} OH \\ ONa. \end{cases} + CO + H_2O.$$

The water produced is, as before, retained by the excess of sulphuric acid.

This process easily yields considerable quantities of pure carbonic oxide, and is the best method to employ, now that formic acid is artificially prepared in large quantities.

Carbonic oxide is an indifferent substance in so far that it neither unites with acids nor with bases to form salts. And notwithstanding the tendency of the unsaturated diad cardon which it contains to pass into saturated tetrad carbon by union with some other element, it neither unites with oxygen, nor with sulphur, or chlorine at the ordinary temperature. Combination with oxygen to form carbonic acid or with sulphur to form carbon oxysulphide : COS, requires a high temperature ; and to produce its compound with chlorine—carbon oxychloride : $COCl_2$—either a high temperature or direct sunlight is necessary.

Although carbonic oxide does not unite with aqueous caustic potash, the solid substance combines easily and completely with the gas when the two bodies are heated up to 100° or over. The sole product of this union is potassic formate :—

$$KOH + CO = \begin{cases} H \\ CO \cdot OK \end{cases}$$

We can, therefore, obtain carbonic oxide from formic acid by the abstraction of a molecule of water, and reconvert the gas into formic acid by the action of caustic potash.

If carbonic oxide is led into a concentrated hydrochloric acid solution of cuprous chloride : Cu_2Cl_2, it is absorbed in considerable

quantities, and a crystalline compound is produced which contains the elements of cuprous chloride, carbonic oxide, and water.

CARBON OXYCHLORIDE (**Carbonyl Chloride**).

Composition: $COCl_2$.

This compound, also known as *phosgene gas*, because formed by the action of light, may be considered as carbonic acid in which one atom of oxygen has been displaced by two atoms of chlorine, and has the same relation to this substance as sulphuryl chloride (p. 164) to sulphuric anhydride. It is produced, without explosion, when equal volumes of carbonic oxide and chlorine are exposed to direct sunlight, the volume of the mixed gases diminishing to one half.

Carbon oxychloride is a colourless gas of peculiar, suffocating odour, easily condensed in an ordinary freezing mixture to a colourless liquid, with a specific gravity of 1·43, and boiling at +8°. The specific gravity of the gas is 3·46, and its molecular weight $3{\cdot}46 \times 28{\cdot}88 = 99{\cdot}9$, corresponding to the formula: $COCl_2$. Its composition is also proved from the fact that two volumes (one molecule) of carbonic oxide and two volumes of chlorine produce two volumes of the gas:—

$$\underset{\text{2 vols.}}{CO} + \underset{\text{2 vols.}}{Cl_2} = \underset{\text{2 vols.}}{COCl_2}$$

In contact with water it is at once decomposed into carbonic acid and hydrochloric acid.

OXALIC ACID.

$$\textit{Composition}: \begin{cases} CO\cdot OH \\ CO\cdot OH \end{cases}$$

Oxalic acid occurs in nature as the acid potassium salt in the various kinds of sorrel and other plants, and also in combination with lime as calcium oxalate.

It crystallizes in colourless rhombic prisms with two molecules of water of crystallization, which can be easily expelled on heating. Oxalic acid possesses a strong acid reaction, and is tolerably

soluble both in water and alcohol. Nine parts of water dissolve one of the acid at the ordinary temperature, and a much larger quantity when hot. When the anhydrous acid is heated above 100°, a portion sublimes unchanged, but the greater part is decomposed into carbonic acid and formic acid :—

$$\begin{cases} CO \cdot OH \\ CO \cdot OH \end{cases} = CO_2 + \begin{cases} H \\ CO \cdot OH \end{cases}$$

which latter then further decomposes into water and carbonic oxide.

Oxalic acid is not now obtained, as formerly, from the acid juice of the sorrel, nor by the expensive process of oxidizing cane-sugar with nitric acid, but is exclusively prepared from some form of cellulose, generally sawdust. The sawdust is mixed with caustic potash, to which a certain, not too large a quantity of caustic soda may be added, and the mass heated until it fuses. The cellulose is thus destroyed—oxidized—with evolution of hydrogen, and a large part of its carbon converted into oxalic acid, which unites with the potassium and sodium.

The fused mass is then extracted with water, neutralized with hydrochloric acid, and mixed with a solution of calcium chloride. The insoluble calcium oxalate which is thus produced is filtered off, suspended in water, and digested with the requisite quantity of sulphuric acid. By this means slightly soluble calcium sulphate (gypsum) is formed, and the oxalic acid remaining in solution is deposited on evaporation ; the crude acid being afterwards purified by repeated crystallization.

Of theoretical interest is the fact that oxalic acid can be directly obtained from carbonic acid by reduction. If dry carbonic acid is led over potassium amalgam, a brisk reaction takes place, and potassium oxalate is formed. The mercury of the potassium amalgam undergoes no change, but serves simply as a diluent :—

$$2CO_2 + 2K = \begin{cases} CO \cdot OK \\ CO \cdot OK \end{cases}$$

Oxalic acid is a dibasic acid, and is a chemical compound of two atoms of the monad radical *oxatyl* : $CO \cdot OH$, just as a molecule of hydrogen consists of two separate atoms. The oxalates are mostly insoluble in water. One of the most insoluble is calcium oxalate, which is not even dissolved by acetic acid, and which serves, therefore, for the detection and estimation of oxalic acid (and calcium).

Oxalic acid in its relations to nitric acid is very stable; even when the two are boiled together it is only slowly oxidized to carbonic acid. Other oxidizing agents, as potassium permanganate or manganese peroxide, convert it easily and completely into carbonic acid and water.

On heating oxalic acid to the point when it begins to sublime, a portion of it is converted into carbonic acid and formic acid, as previously explained; and if the oxalic acid is dissolved in aqueous glycerine, and then heated to 100°, the change into these two substances is so complete and easy, that this method is employed as the best for preparing formic acid.

The conversion of oxalic acid into carbonic acid, carbonic oxide, and water, when heated with concentrated sulphuric acid, has been already referred to (p. 295).

Oxamic Acid and Oxamide.

Just as the hypothetical carbonic acid becomes carbamic acid when one of its atoms of hydroxyl is displaced by amidogen, and carbamide on displacement of both atoms by the same radical, so the same change in oxalic acid produces oxamic acid and oxamide respectively:—

Oxalic acid	$\begin{cases} CO{\cdot}OH \\ CO{\cdot}OH \end{cases}$
Oxamic acid	$\begin{cases} CO{\cdot}NH_2 \\ CO{\cdot}OH \end{cases}$
Oxamide	$\begin{cases} CO{\cdot}NH_2 \\ CO{\cdot}NH_2 \end{cases}$

Oxamic Acid: $\begin{cases} CO{\cdot}NH_2 \\ CO{\cdot}OH \end{cases}$ is a white, crystalline powder, slightly soluble in water. It is produced by heating acid ammonium oxalate:—

$$\begin{cases} CO{\cdot}ONH_4 \\ CO{\cdot}OH \end{cases} = \begin{cases} CO{\cdot}NH_2 \\ CO{\cdot}OH \end{cases} + H_2O;$$

or by boiling oxamide with aqueous ammonia:—

$$\begin{cases} CO{\cdot}NH_2 \\ CO{\cdot}NH_2 \end{cases} + H_2O = \begin{cases} CO{\cdot}NH_2 \\ CO{\cdot}ONH_4 \end{cases}$$

and is separated from the solution of its ammonium salt thus obtained by hydrochloric acid.

Oxamic acid is a monobasic acid, and is easily dissolved by

alkalies, but when boiled with these it takes up the elements of water and is converted into oxalic acid and ammonia. Boiled with water, it gives acid ammonium oxalate.

Oxamide: $\begin{cases} CO\cdot NH_2 \\ CO\cdot NH_2 \end{cases}$ is a white crystalline powder, tasteless and odourless, insoluble in cold water or alcohol, and only slightly dissolved by these liquids when hot. It is produced when normal ammonium oxalate is heated :—

$$\begin{cases} CO\cdot ONH_4 \\ CO\cdot ONH_4 \end{cases} = \begin{cases} CO\cdot NH_2 \\ CO\cdot NH_2 \end{cases} + 2H_2O.$$

It is, however, better prepared from an organic compound of oxalic acid—oxalic ether, a colourless liquid with pleasant ethereal odour and insoluble in water[1]—by shaking it with aqueous ammonia. The oily liquid gradually disappears, and a crystalline powder of oxamide takes its place, with the simultaneous formation of alcohol :—

$$\underset{\text{Oxalic ether}}{\begin{cases} CO\cdot OC_2H_5 \\ CO\cdot OC_2H_5 \end{cases}} + 2NH_3 = \underset{\text{Oxamide}}{\begin{cases} CO\cdot NH_2 \\ CO\cdot NH_2 \end{cases}} + \underset{\text{Alcohol}}{2C_2H_5\cdot OH}$$

When carefully heated, oxamide may be sublimed, but quick heating decomposes it into various products, among which cyanogen may be recognized by its odour. Boiling with aqueous alkalies changes it into oxalic acid and ammonia.

CARBON DISULPHIDE.

Composition: CS_2.

This compound, the anhydride of a sulpho-acid corresponding to carbonic acid, was discovered by Lampadius towards the end of the preceding century. It is produced in a precisely similar method to carbonic acid—viz. by burning carbon in sulphur gas. A considerably higher temperature is, however, necessary to cause carbon to burn in sulphur than in oxygen.

Carbon disulphide is a colourless, mobile, very volatile liquid, insoluble in water, in which it sinks, refracting light strongly, and

[1] Oxalic ether is prepared by distilling a mixture of dry oxalic acid and absolute alcohol.

possessing an unpleasant ethereal odour. It has a specific gravity of 1·29, boils at 46°, and is miscible with alcohol and ether in all proportions. It is very inflammable, and burns with a bluish flame to carbonic acid and sulphurous acid, with the separation of sulphur if the air supply is insufficient.

Carbon disulphide is prepared by heating freshly glowed wood-charcoal in large tubulated earthenware retorts to bright redness in a suitable furnace, and dropping in pieces of sulphur from time to time. The neck of each retort is connected air-tight with a large receiver in which the uncombined sulphur condenses, and from this the carbon disulphide vapours are led through well-cooled condensers. The crude product contains sulphur, sulphuretted hydrogen, and other impurities, imparting to it a very unpleasant odour, and from which the carbon disulphide cannot be completely freed even by repeated free redistillation. It may be effectually purified by shaking with mercury and with mercuric chloride, and then distilling.

Carbon disulphide is employed for numerous technical purposes, and is now manufactured on a large scale and sold at a low price. It is an excellent solvent for many substances—*e.g.* for iodine, sulphur, phosphorus, fatty and ethereal oils, resins, &c.—and in consequence of this property is largely used to impregnate india-rubber with sulphur in the manufacture of vulcanised rubber, to free the finer kinds of wool from fat, and to extract fatty oils from seeds containing them.

Air containing small quantities of the vapour of carbon disulphide, when respired, acts in a similar manner to chloroform and produces insensibility ; in larger quantities it is poisonous. At the same time carbon disulphide possesses strong antiseptic properties ; it prevents the putrefaction of meat, and stops the processes of fermentation.

Pure carbon disulphide exposed to sunlight soon becomes of a yellow colour and acquires the unpleasant odour of the crude substance. After some time it deposits a brown amorphous substance, which apparently has the composition of carbon monosulphide : CS, and which is insoluble in carbon disulphide and most other liquids. It is probable that the light decomposes the carbon disulphide into sulphur and the still unknown monosulphide, which then polymerises to form this brown substance.

Dry chlorine gas decomposes carbon disulphide with formation of disulphur dichloride and carbon tetrachloride.

Carbon disulphide is the anhydride of a dibasic sulpho-acid—*sulphocarbonic acid*: $CS\begin{cases}SH\\SH\end{cases}$—and as such can unite with aqueous solutions of sodium or potassium sulphides, or other sulphides soluble in water, to form sulphosalts—*e.g.* with potassium sulphide to form the compound: $CS\begin{cases}SK\\SK\end{cases}$—potassium sulphocarbonate.

The sulphocarbonates can only be obtained in the solid form with difficulty, as they very easily decompose. The potassium compound separates out from its concentrated solution in yellow deliquescent crystals, containing water.

Aqueous alkalies also dissolve carbon disulphide and produce a mixture of sulphocarbonate and carbonate:—

$$3CS_2 + 6KOH = 2CS\begin{cases}SK\\SK\end{cases} + CO\begin{cases}OK\\OK\end{cases} + 3H_2O.$$

If aqueous ammonia is used, ammonium sulphocarbonate: $CS\begin{cases}SNH_4\\SNH_4\end{cases}$ is also produced, together with ammonium sulphocarbamate: $CS\begin{cases}NH_2\\SNH_4\end{cases}$ and ammonium sulphocyanate: $CSN \cdot NH_4$.

Alcoholic potash when warmed with carbon disulphide dissolves considerable quantities, and after a short time the liquid almost solidifies to a mass of small yellow crystals. This compound is not potassium sulphocarbonate, but is the potassium salt of an organic acid, termed xanthogenic acid.

If a sulphocarbonate is mixed with alcohol and then hydrochloric acid added, free sulphocarbonic acid: $CS\begin{cases}SH\\SH\end{cases}$ separates as a dark yellow oil, with a disagreeable odour. The acid readily decomposes into carbonic disulphide and sulphuretted hydrogen.

CARBON OXYSULPHIDE.

Composition: COS.

This compound, which may be considered as carbonic acid in which one atom of oxygen is displaced by sulphur, and is therefore the intermediate compound between carbonic acid and carbon disulphide, is a colourless gas, without odour when pure, combus-

tible and easily inflamed. Water dissolves its own volume of the gas, but decomposes it on standing into carbonic acid and sulphuretted hydrogen.

Carbon oxysulphide is found in some mineral waters, and may be artificially prepared by leading carbonic oxide with excess of sulphur vapour through a glass tube heated to low redness, or by heating a mixture of sulphuric anhydride and carbon disulphide. The best method for its preparation consists in heated potassium sulphocyanate with moderately dilute sulphuric acid. There are then produced, besides carbon oxysulphide, acid ammonium sulphate and acid potassium sulphate as secondary products, together with some hydrocyanic acid and sulphuretted hydrogen :—

$$CSNK + 2SO_2\begin{cases}OH\\OH\end{cases} + H_2O = COS + SO_2\begin{cases}OH\\ONH_4\end{cases} + SO_2\begin{cases}OH\\OK\end{cases}$$

Alkalies, like water, decompose carbonic oxysulphide, with formation of carbonic acid and sulphuretted hydrogen ; thus, with potash the change is as follows :—

$$COS + 4KOH = CO\begin{cases}OK\\OK\end{cases} + K_2S + 2H_2O.$$

A second compound isomeric with carbonic oxysulphide, of the composition : CSO, may exist, but has not yet been prepared.

COMPOUNDS OF CARBON WITH HYDROGEN.

Carbon and hydrogen, although they have little attraction for one another in the free state, unite together to form a large series of compounds—the so-called hydrocarbons. Nearly all these belong to organic chemistry, and we can here only refer to two of the simplest—viz. methane and ethylene.

METHANE, or MARSH GAS.

Composition: CH_4.

This, the most important compound of carbon and hydrogen, is a colourless, odourless gas, insoluble in water, and burning in the air with a pale, non-luminous flame. Its specific gravity is 0·55, and its molecular weight, therefore, $0·55 \times 28·88 = 15·9$, corresponding to the above composition. Its low specific gravity gave rise to its old name *light carburetted hydrogen*, as distinguished from *heavy carburetted hydrogen*, or ethylene.

Methane is found in nature as a product of the decomposition of organic substances out of contact with air—for example, by the putrefaction of vegetable matter at the bottom of stagnant pools and marshes. The *marsh gas* thus produced rises to the surface in large bubbles when the mud is stirred up with a stick. This gas is, of course, not pure methane, but contains, besides, some carbonic acid and nitrogen—the former being produced by decomposition, the latter from the air dissolved in the water.

Methane is set free in immense quantities in some coal-mines, owing to partial decomposition of the coal. A mixture of this methane with atmospheric air, which is often produced in such mines, explodes when ignited, even more violently than a mixture of hydrogen and air. Two volumes of hydrogen, requiring for its combustion one volume of oxygen, produce two volumes of water-gas; but two volumes of methane, requiring four volumes of oxygen, produce, on ignition, two volumes of carbonic acid, and four volumes of water-gas:—

$$\underset{2\text{ vols.}}{CH_4} + \underset{4\text{ vols.}}{2O_2} = \underset{2\text{ vols.}}{CO_2} + \underset{4\text{ vols}}{2H_2O}.$$

With a falling barometer—*i.e.* with reduced air pressure, large quantities of this methane pass from cavities in the coal into the workings of the mines, and, mixing with the air, produce an explosive mixture (fire-damp), which is readily ignited by the lamp of the miner, and then produces those fearful explosions by which so many lives are annually lost.[1]

The safety lamp constructed by *Davy* to avoid these explosions consists of a small oil-lamp completely surrounded by wire gauze, and its action depends upon the fact that an ignited and explosive gaseous mixture when passing through wire gauze has its tempera-

[1] See Appendix.

ture lowered below its point of ignition by the conductivity of the metal for heat, and, therefore, does not burn on the other side of the gauze. Various unforeseen difficulties have, however, prevented its general application, and it is often rendered useless by the miner opening the gauze casing for purposes of his own.

Methane is produced, not only by slow putrefaction, but also by the destructive distillation of coal, and is therefore one of the chief constituents of coal-gas. The well-known lightness of coal-gas and its use for filling balloons are due to this methane, and to the hydrogen which it contains. Other carbon compounds also yield methane when strongly heated. Thus, the vapour of ordinary alcohol: C_2H_6O, when driven through a red-hot iron tube, yields considerable quantities of methane, mixed however with carbonic acid:—

$$2C_2H_6O = 3CH_4 + CO_2.$$

Methane may be obtained fairly pure by strongly heating an intimate mixture of dry sodium acetate and caustic soda, or better soda-lime[1] in a tube of hard glass. The products are then methane and sodium carbonate:—

$$\underset{\text{Sodium acetate}}{\begin{cases} CH_3 \\ CO\cdot ONa \end{cases}} + NaOH = CH_4 + CO(ONa)_2.$$ [2]

Chemically pure methane can only be obtained from an organic compound called zinc methyl: $Zn(CH_3)_2$, and which is distinguished by its great tendency to unite with oxygen. This body is a colourless, volatile liquid, which catches fire at once when exposed to the air and decomposes water with almost explosive violence. If zinc methyl is boiled in a glass flask, out of contact with air, and its vapour then passed into water, it is at once decomposed into methane and zinc hydrate, the latter separating out as a white, gelatinous solid, or remaining dissolved as zinc chloride, if hydrochloric acid has been previously added to the water:—

$$\underset{\text{Zinc methyl}}{Zn(CH_3)_2} + 2H_2O = 2CH_4 + Zn(OH)_2.$$

Methane is a perfectly indifferent compound, and unites with no other substance without decomposition. Sulphuric, nitric, or phosphoric acid are without action on it, and even the powerful oxidizing mixture of potassium dichromate and sulphuric acid, as

[1] Quick-lime which has been slaked with caustic soda solution instead of with water.—ED.

[2] See Appendix.

well as caustic potash, leave it entirely unchanged. Chlorine is without action upon it in the dark, but if a mixture of the two gases is led into vessels exposed to direct sunlight, one or more atoms of hydrogen, according to the volume of the chlorine, are abstracted from the methane to form hydrochloric acid, while the place of the hydrogen atoms in the methane molecule is taken by an equal number of atoms of chlorine. The end product of the action of chlorine on methane contains no hydrogen, but as many atoms of chlorine as were originally present of hydrogen.

The composition of these different chlorine *substitution-products* of methane is as follows :—

Methane (Methyl hydride)	CH_4
Monochlormethane (Methyl chloride) . .	CH_3Cl
Dichlormethane (Methylene chloride) . .	CH_2Cl_2
Trichlormethane (Chloroform)	$CHCl_3$
Tetrachlormethane (Carbon tetrachloride) .	CCl_4

These compounds belong to organic chemistry.

Ethylene, also known as **Olefiant gas**, because it forms an oily liquid with chlorine, contains in its molecule the same quantity of hydrogen as methane but twice as much carbon, and has, therefore, the *composition*: C_2H_4. Ethylene is a colourless gas, of peculiar odour, slightly soluble in water, and condensed to a liquid under considerable pressure and at a low temperature. Its specific gravity is 0·968, and its molecular weight $0{\cdot}968 \times 28{\cdot}88 = 28{\cdot}00$, corresponding, therefore, to the formula: C_2H_4. It is easily inflammable and burns with a bright luminous flame.

Ethylene is easily obtained from common alcohol. This compound, which, at a low red heat, breaks up into carbonic acid and methane, is converted by the abstraction of the elements of water into ethylene. Concentrated sulphuric acid is best employed for this purpose. Four parts by weight of the acid are gradually added to one part of strong alcohol in a large flask provided with a delivery tube. The mixture is then gently heated, and as soon as its temperature has risen to about 150°, a copious evolution of ethylene begins. To free the gas from alcohol carried over with it, it is passed through a wash-bottle containing water, and to remove the sulphurous anhydride, produced towards the end of the operation, a second wash-bottle containing caustic potash is used.

The process is represented by the following equation, the sulphuric acid remaining unchanged :—

$$C_2H_6O = C_2H_4 + H_2O. \qquad \text{(See App.)}$$

If ethylene and chlorine are mixed in a large vessel and exposed to diffuse daylight (in direct sunlight the mixture would explode), the two gases unite to produce a colourless, heavy oil, of pleasant ethereal odour, and having the composition : $C_2H_4Cl_2$—*ethylene dichloride.* Ethylene also unites directly with bromine, producing *ethylene dibromide*: $C_2H_4Br_2$, a liquid with similar properties to the chloride. The corresponding iodide : $C_2H_4I_2$, is a crystalline solid, but less stable.

Ethylene behaves, therefore, like a diad element, and unites without change with two atoms of chlorine, &c., just like copper, zinc, and other metals.

If a glass cylinder is half filled with ethylene over water, then an equal volume of chlorine added and a burning taper quickly brought near the open end of the jar, the mixture catches fire, and burns with an exceedingly smoky flame. The products are hydrochloric acid and carbon. Even when excess of chlorine is present no chloride of carbon is formed, a proof that the attraction of carbon for chlorine is not sufficient to cause the elements to unite directly with one another.

Since the molecule of ethylene contains two atoms of carbon, instead of one, like methane, it requires a larger quantity of oxygen to burn it than this gas. Two volumes of ethylene require six volumes of oxygen for complete combustion, and produce four volumes of carbonic acid, and four of water-gas :—

$$\underset{\text{2 vols.}}{C_2H_4} + \underset{\text{6 vols.}}{3O_2} = \underset{\text{4 vols.}}{2CO_2} + \underset{\text{4 vols.}}{2H_2O}.$$

Ethylene and oxygen mixed in this proportion—*i,e.* 1 : 3, explode violently when ignited, and easily burst a thin glass flask which has been carefully enveloped in towels.[1]

At first sight it seems strange that ethylene should burn with a flame so much more luminous than methane, although the latter gas contains half as much carbon and the same quantity of hydrogen ; and connected with this point is the question, Upon what does the luminosity of a flame depend ?

Experiment teaches us that under normal conditions only those flames are luminous which contain a glowing solid body. The

[1] See Appendix.

scarcely luminous hydrogen and oxy-hydrogen flames give out an intense light if a solid substance—*e.g.* platinum, lime, &c.—is strongly heated in them.

In the same way the flame of burning ethylene contains a solid substance—*i.e.* carbon. And the presence of carbon in the flame may be readily proved by holding a cold, white porcelain dish in it. Those parts of the dish which come into contact with the inner parts of the flame receive a black deposit of soot, just as burning arsine deposits brown arsenic on a piece of cold porcelain (p. 232).

The constitution of a luminous flame is not, however, so simple as might be thought from the above statements. Three parts may be distinguished in every luminous flame: an innermost and cold portion, an intermediate and luminous, and a less luminous and hot external mantle, as is illustrated in fig. 57. The gas which streams out of the burner at A does not at once enter into combustion, because no oxygen is present with which it can combine. The inner cone, *a'a*, consists therefore of unburnt gas, and is cold. This may be readily proved by stretching a fine platinum wire across the flame, which will become red-hot at the two sides of the flame but remain dark, because cold, in the centre.

Fig. 57.

The oxygen which rapidly diffuses from the exterior to the interior portions of the flame not only causes the gases to burn in the exterior mantle, but, by the high temperature produced during this combustion, decomposes *the unburnt gases in the interior of the flame.* The decomposition which is thus brought about is the same as that which ethylene suffers when passed through a red-hot tube out of contact with the air. It is then changed into methane and carbon: $C_2H_4 = CH_4 + C$, and it is this carbon which is so liberated, and which is heated in the interior mantle of the flame *f, e, g* (fig. 57) by the external burning gases, that gives the flame its luminosity. *Ethylene is not, therefore, directly burnt in the flame, but rather the* products into which it has been changed—viz. methane and carbon.

The same process goes on when a candle burns. A burning body brought near to the wick produces the same changes in the fat or wax as destructive distillation, and forms combustible gases which catch fire. The heat of the flame then continually melts

the solid fat at its base, which is sucked up by the porous wick to the flame to be decomposed and burnt. It is not, however, the fat itself which burns, but the gaseous products into which it has been decomposed by the heat of the flame. The further course of the combustion then resembles that of ethylene.

A luminous flame may easily be made non-luminous if the combustible gases are mixed with enough oxygen to completely oxidize the whole of the carbon. This can either be done by blowing air or oxygen into the luminous flame (as in the blowpipe), or by previously mixing the gas with air. In the *Bunsen burner* a mixture of gas and air is obtained in the following manner. The gas is allowed to issue from a small opening over which is screwed a brass tube, with two openings at the base, to admit the air. The gas and air then mix so thoroughly in ascending the tube, that the mixture burns at the top of the tube without smoke or luminosity.

The temperature of a flame is sometimes judged from the intensity of the light which it emits, and although this may to a certain extent be true for solid bodies (iron is hotter when white-hot than when red-hot, and when brightly glowing than when feebly glowing), in the case of burning gases luminosity and temperature are often inversely proportional to one another.

The non-luminous flame of coal gas burning in a Bunsen burner is much hotter than the luminous flame of the same gas burnt in the usual manner. In the latter case the interior of the flame contains unburnt carbon, but in the former *all* the constituents of the gas are at once burnt. For the same reason the external non-luminous mantle *d*, *b*, *c*, of the gas flame (fig. 57) is much hotter than the interior luminous portion.

CARBON TETRACHLORIDE.

Of the numerous compounds of carbon and chlorine which are more closely allied to organic than inorganic compounds, we shall here only briefly allude to the most important and at the same time the simplest.

Composition: CCl_4.

Carbon tetrachloride is a colourless liquid sinking in water, but not mixing with it. Its specific gravity is 1·6, and its boiling

point 77°. The liquid possesses a pleasant, ethereal odour, and when breathed acts as an anæsthetic like chloroform.

Carbon tetrachloride cannot be obtained by the direct union of carbon and chlorine, but is readily produced from carbon disulphide when this liquid is mixed with an excess of dry chlorine and exposed to the light. A quicker method of preparing it consists in passing chlorine which has bubbled through warm carbon disulphide through a red-hot porcelain tube, or by treating this last-named liquid with antimony pentachloride in the presence of chlorine. In all cases the carbon disulphide is converted into carbon tetrachloride and disulphur dichloride. These mixed liquids are then digested with caustic soda, which decomposes the latter, and the carbon tetrachloride then distils over with water vapour on heating. It has already been mentioned (p. 306) that carbon tetrachloride can also be obtained from methane.

Carbon tetrachloride is a very stable compound ; it is distinguished from most other inorganic chlorides by the fact that when boiled with aqueous potash it remains unchanged. Its alcoholic solution is not decomposed when a similar solution of silver nitrate is added to it – silver chloride is not precipitated.

If gaseous carbon tetrachloride is led through a red-hot tube it is decomposed into chlorine, and a liquid chloride of carbon containing only one half as much chlorine. The molecule of this compound does not, however, consist of one atom of carbon and two of chlorine, but contains two atoms of carbon united with four atoms of chlorine, and has, therefore, a similar composition to the tetrachloride as ethylene has to methane :—

Methane . . .	CH_4	Tetrachlormethane . .	CCl_4
Ethylene . . .	C_2H_4	Tetrachlorethylene . .	C_2Cl_4

This tetrachlorethylene, like ethylene, unites with two atoms of chlorine, and yields a compound corresponding to ethylene dichloride :—

Ethylene dichloride : $C_2H_4Cl_2$.

Tetrachlorethylene dichloride (carbon hexachloride) : C_2Cl_6.

Carbonic hexachloride is a volatile crystalline solid with an odour resembling that of camphor, and which, like camphor, easily sublimes on the walls of the vessels in which it is kept.

Carbon Tetrabromide : CBr_4, closely resembles the tetrachloride in its preparation and properties

CYANOGEN.

Cyanogen is the name given to a compound consisting of one atom of carbon and one atom of nitrogen, which is so similar in its properties to an element, and especially to the halogens, that it would certainly have been considered as such if it were not possible to produce it from its constituents, and to again decompose it into them.

Cyanogen was discovered by Gay-Lussac in 1815; its name is derived from κυάνεος, blue, because it is a constituent of Prussian blue, which can be prepared from it.

Composition: CN.

The molecule of cyanogen consists of two atoms,[1] just as the molecule of hydrogen also contains two atoms, and the composition of its molecule is therefore expressed by the formula: $CN \cdot CN$, or $(CN)_2$. Cyanogen may also be still more briefly expressed by the symbol: Cy.

Cyanogen is a colourless gas of a peculiar odour, resembling hydrocyanic acid, and with a specific gravity of 1·8. This gives a molecular weight of $1{\cdot}8 \times 28{\cdot}88 = 52$, corresponding to the formula $(CN)_2$. At a low temperature, and under a strong pressure, it may be condensed to a colourless liquid, boiling at $-20°$, or even to a crystalline solid. Water dissolves about $4\frac{1}{2}$ times its volume; alcohol considerably more. It is easily inflammable, and burns with a beautiful flame of a peach-blossom colour, which, as neither glowing carbon nor nitrogen possess this colour, must be peculiar to glowing cyanogen.

Cyanogen is prepared by heating mercuric cyanide. This white crystalline compound, which is easily soluble in water, is obtained by dissolving mercuric oxide in excess of aqueous hydrocyanic acid, and then crystallizes out on evaporating the clear solution.

[1] Strictly, it is, of course, incorrect to speak of an atom of cyanogen, since it is not, like the atoms of the elements, chemically indivisible. It is, however, convenient to extend the word atom to the compound radicals of organic and inorganic chemistry, which play the part of elementary substances, instead of coining a new word such as *semi-molecule*. When we speak of an atom of cyanogen, ammonium, amidogen, or ethyl, we do not mean an indivisible quantity of the substance, but such a quantity which exactly corresponds to the elementary atoms and can displace them in chemical compounds.

After being freed from traces of water which it contains, it breaks up when heated to low redness into mercury and cyanogen, just as mercuric oxide decomposes under similar circumstances into mercury and oxygen. The gas can be collected over mercury. A portion of the cyanogen remains behind in the tube as an amorphous brown substance called *paracyanogen*, which has the same composition as cyanogen but a higher molecular weight, and of which it is therefore a polymeric compound.

No compound of cyanogen with oxygen or sulphur is known in the free state, and it can only be brought into combination with these substances indirectly. With the halogens it combines at once as soon as they liberate it from its compounds with hydrogen (hydrocyanic acid) or with the metals (potassium or mercuric cyanide.)

Potassium and sodium burn in cyanogen like they burn in chlorine, and unite directly with the gas, producing potassium or sodium cyanide. These compounds are distinguished by their stability; they can be heated to redness, out of contact with the air, without decomposition.

Although carbon and nitrogen never unite directly with one another when heated together alone, they may be made to combine in the presence of a third substance which readily unites with cyanogen—*e.g.* potassium. Potassium carbonate and carbon, when heated to bright redness, form carbonic oxide and potassium, and if nitrogen is led over the glowing mixture, a compound of potassium and cyanogen is produced, called potassium cyanide: KCy, a white solid, soluble in water like potassium chloride, and, like this salt, yielding, when decomposed by sulphuric acid, an acid—hydrocyanic acid—corresponding to hydrochloric acid.

The same conditions necessary for the production of potassium cyanide are also present when nitrogenous organic substances, such as blood, hair, horn, are mixed with potassium carbonate and heated. Under these circumstances, the nitrogen and carbon of the organic substances unite with the potassium to form potassium cyanide. This process is that by means of which cyanogen compounds are manufactured on a large scale. The first compound always prepared is the so-called *yellow prussiate*, or potassium ferrocyanide, which may be considered as a double cyanide of potassium and iron: $4KCy,Fe''Cy_2$, and which will be more fully discussed under the compounds of iron. It is also produced when an aqueous solution of potassium cyanide acts upon powdered ferrous sulphide; a portion of the potassium cyanide is then decom-

posed, and forms potassium sulphide and ferrous cyanide. From its solution in water it crystallizes in large yellow tablets.

Potassium ferrocyanide forms the starting-point for the preparation of all the other cyanogen compounds—*e.g.* hydrocyanic acid, potassium cyanide, potassium cyanate, &c.

HYDROCYANIC ACID. (**Prussic Acid.**)

Composition: HCN or HCy.

This compound, well known on account of its highly poisonous character, is, when completely anhydrous, a colourless, mobile, volatile liquid, miscible with water in all proportions. It possesses a strong stupefying odour, and has a specific gravity of 0·7. Its boiling-point is 27°, and at −15° it solidifies to a crystalline solid. It is easily combustible.

Anhydrous hydrocyanic acid may be prepared in the same way as hydrochloric acid by pouring concentrated sulphuric acid on to potassium cyanide, but the reaction is much too violent, and, on account of the poisonous nature of the gas, far too dangerous to be employed. It is much better to first prepare the aqueous acid and then to abstract water from it. For the same reason it is better to employ for the preparation of the dilute acid not potassium cyanide, but its compound with ferrous cyanide—*i.e.* potassium ferro-cyanide.

To obtain the dilute aqueous acid, 10 parts of powdered potassium ferrocyanide are covered with a mixture of 6 parts of sulphuric acid and 30 parts of water in a tubulated retort with its neck inclined upwards. The end of the neck of the retort is connected by a cork and a bent tube with a condenser, the other end of which dips in a receiver carefully cooled in ice, and in which it is best to place a little water at the commencement. The mixture in the retort is then gradually brought to boiling, when a portion of the water-vapour condenses in the neck of the retort, while the volatile hydrocyanic acid passes over to the well-cooled receiver. The whole apparatus should be placed in a good upward draught, and every precaution taken, not only in the preparation of this highly poisonous volatile compound, but also in all experiments made with it afterwards.

In order to prepare the anhydrous compound from its aqueous solution, a flask which is about one-third filled with the latter is placed in ice and small pieces of fused calcium chloride gradually dropped in, which unites with the water and partially liquefies. On no account must the aqueous acid be poured on to the calcium chloride, as the heat produced by the union of the latter with the water would drive off large quantities of gaseous hydrocyanic acid. After a few hours, the flask is attached to a long condenser and a receiver immersed in a freezing mixture, and then gently heated on a water bath. Anhydrous hydrocyanic acid then distils over as a clear, transparent liquid.

Aqueous, and still more anhydrous hydrocyanic acid, undergoes a change when kept for some time in closed vessels, with the separation of a brown amorphous substance, known as *parahydrocyanic acid*, and probably a polymeric compound of hydrocyanic acid. The decomposition is usually accompanied with an evolution of gas, which sometimes exerts sufficient pressure to destroy the vessels in which it is preserved. It has been found that the addition of a few drops of hydrochloric acid materially diminishes this spontaneous decomposition.

Hydrocyanic acid is one of the most powerful poisons known. A few drops of the strong aqueous acid produce almost instantaneous death. Its vapour is also highly poisonous when respired; a pigeon dies in about half a minute when breathing air mixed with the vapour from anhydrous hydrocyanic acid, even when the temperature of the liquid is as low as $0°$.

Very largely diluted with water, hydrocyanic acid is a valuable medicine. The strength prescribed by the 'British Pharmacopœia' is a 2 per cent. solution; a 3 per cent. solution is also sometimes used under the name Scheele's prussic acid. Bitter almonds, and the kernels of cherries, plums, &c., as well as the leaves of the common or cherry laurel, contain a crystalline organic compound of complex composition, called amygdaline. When these substances are crushed and moistened with water, the amygdaline comes into contact with a ferment (emulsine) which they also contain, and is then decomposed as sugar is decomposed by yeast. One of the products of this decomposition is hydrocyanic acid, which, when the water is afterwards distilled, passes over with the water-vapour into the receiver. The preparations known as bitter-almond-water and laurel-water are obtained in this way.

Hydrocyanic acid is so weak an acid that it does not even red-

den blue litmus paper, and is expelled by carbonic acid from its compounds with the alkalies. For this reason, potassium cyanide when exposed to the air smells strongly of hydrocyanic acid.

In many of its reactions, it shows a similarity with the hydrogen compounds of the halogens—for example, when mixed with a solution *of silver nitrate it gives a white, curdy precipitate of silver cyanide,* which, like silver chloride, is insoluble in nitric acid but dissolves in ammonia. Silver chloride may, however, be at once distinguished *from silver cyanide if heated; the former compound* simply melts, but the latter is decomposed into silver and cyanogen gas. As potassium chloride unites with platinic chloride to form a stable crystalline double compound, so also potassium cyanide unites with nearly all the metallic cyanides, and produces from these insoluble substances soluble crystalline double cyanides, of which the stable potassium ferrocyanide may be taken as an example.

Chlorine easily decomposes hydrocyanic acid, uniting with its two constituents to form cyanogen chloride and hydrochloric acid.

In order to detect hydrocyanic acid in a liquid, advantage is taken of the readiness with which Prussian blue may be formed *from it. Prussian blue may be considered as a double compound* of ferric and ferrous cyanides, $Fe'''Cy_3$ and $Fe''Cy_2$, and although insoluble in water and dilute acids, is not produced when a mixture of a ferrous and ferric salt is added to the aqueous acid. If, however, this mixture is made alkaline with caustic potash, potassium ferrocyanide and a mixture of ferrous and ferric hydrates are produced, and this, when acidulated with hydrochloric acid, forms Prussian blue due to the union of the potassium ferrocyanide with the ferric chloride.

Cyanogen is a monad radical, and is to be considered as a compound of triad nitrogen with tetrad carbon ($C \equiv N$), two such groups uniting to form a molecule of ordinary cyanogen

$$-C \equiv N \quad + \quad -C \equiv N \quad = \quad \begin{matrix} C \equiv N \\ | \\ C \equiv N \end{matrix}$$

Hydrocyanic acid, which can be obtained in small quantity by submitting a mixture of cyanogen (C_2N_2) and hydrogen to the electric discharge, might have either of the two formulæ :—

$$H - C \equiv N \quad \text{or} \quad H - N \equiv C$$

Only one hydrocyanic acid is known, and this has most probably the first constitutional formula, that is, that in which the hydrogen is directly united with carbon.

The different behaviour of some of the mineral cyanides (*e.g.* those of potassium and silver) renders it probable that some are derived from $H - C \equiv N$, and some from $H - N \equiv C$; and there are several cases of isomerism (p. 38) amongst organic cyanides, which are generally explained on a similar supposition.

Thus methyl cyanide, obtained by heating ammonium acetate with phosphoric anhydride,

$$\begin{array}{l} CH_3 \\ | \\ C\begin{smallmatrix}\nearrow O \\ \searrow O-NH_4\end{smallmatrix} \end{array} = \begin{array}{l} CH_3 \\ | \\ C \equiv N \end{array} + 2H_2O,$$

boils at 81°·6 and, on treatment with mineral acids, yields acetic acid and ammonia,

$$CH_3{\cdot}CN + 2H_2O = CH_3{\cdot}COOH + NH_3,$$

whilst methyl isocyanide, which is prepared by treating methyl iodide with silver cyanide,

$$CH_3I + AgNC = AgI + CH_3 - N \equiv C,$$

boils at 59°·6, possesses a characteristic, unbearable odour, and on treatment with mineral acids yields methylamine and formic acid.

$$CH_3NC + 2H_2O = CH_3{\cdot}NH_2 + H{\cdot}CO_2H$$

CYANIC ACID.

Composition: HOCN.

Although cyanogen cannot unite directly with oxygen as it does with chlorine, potassium cyanide can, under favourable circumstances, *easily take up an atom of oxygen and become oxidized to* potassium cyanate. But the compound called cyanic acid does not possess a similar composition to chloric acid; such a compound is, *in fact, as much unknown as compounds of cyanogen corresponding* to perchloric or chlorous acid, or any of the oxides of chlorine. Cyanogen appears in fact to unite with oxygen and hydrogen, or a metal in only one proportion—viz. as cyanic acid; HOCN.

Like hydrocyanic acid, cyanic acid could conceivably exist in two isomeric forms, as shown by the following formulæ:—

$$H-O-C \equiv N \text{ and } H-N=C=O.$$

Difference of opinion still exists as to which formula represents the only known cyanic acid, but the balance of probability seems to be in favour of the first, cyanic acid thus resembling in structure

hypochlorous acid, the atom of chlorine in the latter being replaced by the monovalent CN group. The relation of potassium cyanide to potassium cyanate is best expressed by the following rational formulæ:—

Potassium cyanide . . . . $\begin{matrix} CN \\ | \\ K \end{matrix}$

Potassium cyanate . . . . $O\left\{\begin{matrix} CN \\ K \end{matrix}\right.$

whence it follows that the constitution of cyanic acid is $O\left\{\begin{matrix} CN \\ H \end{matrix}\right.$

The change of potassium cyanide into the cyanate, which takes place so readily, consists therefore of the interpolation of an atom of oxygen between the atom of potassium and the cyanogen group.

Potassium cyanate, a crystalline salt, soluble in alcohol and water, is readily obtained by dropping lead oxide into fused potassium cyanide when the oxide is reduced to metallic lead. The salt will be more fully described under the potassium compounds.

Cyanic acid cannot, however, be set free from this salt by a stronger acid, because whenever the acid comes into contact with water it is at once decomposed into carbonic acid and ammonia:—

$$O\left\{\begin{matrix} CN \\ H \end{matrix}\right. + H_2O = CO_2 + NH_3.$$

Cyanic acid may be obtained by heating a polymeric compound —*cyanuric acid*, $C_3N_3O_3H_3$—which is a white solid, obtained from urea. Cyanuric acid is not itself volatile, but when heated breaks up into cyanic acid, which distils over as a colourless liquid, with an odour resembling acetic acid. If kept below 0° it may be preserved for some time unchanged, but at a few degrees above this temperature the liquid becomes heated, and changes into a white solid, resembling porcelain. This compound, *cyamelide*, is probably a polymer of cyanic acid, and is again converted into it on heating.

The compounds of cyanogen, especially those belonging to organic chemistry, are remarkable for the readiness with which they change into isomeric and polymeric compounds.

SULPHOCYANIC ACID.

Composition: HSCN.

Just as fused potassium cyanide unites readily with oxygen, even that of the air, so also it possesses a strong attraction for sul-

phur. Sulphur dropped into fused potassium cyanide readily combines with it, producing potassium sulphocyanate: KSCN, which from its analogy with potassium cyanate may be considered to possess the same constitution: $S\left\{\begin{matrix}CN\\K\end{matrix}\right.$. The corresponding hydrogen compound, sulphocyanic acid: HSCN, is more stable than cyanic acid; an aqueous solution of it may be prepared by distilling potassium sulphocyanate with dilute sulphuric acid. The anhydrous acid is best obtained by passing dry sulphuretted hydrogen over powdered mercuric sulphocyanate. It then condenses in the receiver as a colourless oily liquid, with a piercing odour, also resembling acetic acid, but when kept for a short time soon decomposes into hydrocyanic acid and a yellow crystalline solid nearly insoluble in water—*persulphocyanic acid*: $C_2H_2N_2S_3$.

Sulphocyanic acid or any soluble sulphocyanate can be at once recognized by the bright red colour which it gives with ferric chloride. This reaction is more delicate than the blue precipitate produced from potassium ferrocyanide and ferric chloride; and ammonium sulphocyanate is the best test for ferric salts.

Chlorides of Cyanogen.

We are acquainted with two polymeric compounds of cyanogen and chlorine, one a colourless gas, and the other a crystalline solid. These compounds appear to stand in the same relation to one another as cyanic acid to cyanuric acid.

Gaseous Cyanogen Chloride: CNCl, is a colourless gas, liquefying at $-14°$, solidifying at $-18°$, and with an exceedingly sharp, tear-producing odour. It is very poisonous. This compound is obtained by the action of chlorine on dilute hydrocyanic acid or on metallic cyanides in the presence of water. The simplest method of preparation is to lead a slow stream of chlorine into a solution of potassium cyanide with twice its weight of water kept cooled in ice. The solution is placed in a retort, which it only fills to about one-fourth, and the neck of the retort is connected with a tube filled partly with bright copper turnings (to absorb the excess of chlorine), and partly with calcium chloride (to retain moisture). This tube communicates with a U-tube placed in a freezing mixture in which the cyanogen chloride condenses. A portion of the volatile compound distils over as soon as it is formed; the residue is afterwards obtained by heating the retort to 50°.

Pure gaseous cyanogen chloride may be preserved unchanged in sealed tubes, but when impure it soon changes into a solid polymeric modification. Water and alcohol dissolve considerable quantities without decomposition, and it can be again expelled from these solutions on heating. Alkalies decompose it. Gaseous cyanogen chloride unites chemically with the chlorides of other elements—*e.g.* of antimony, boron, titanium.

Solid Cyanogen Chloride, probably $C_3N_3Cl_3$, is produced by the action of chlorine on anhydrous hydrocyanic acid in bright sunlight, when it separates out in colourless lustrous crystals. Like the liquid chloride. it has a piercing odour. It melts at 145°, boils at 190°, and is decomposed on boiling with alkalies, or even water, into cyanuric and hydrochloric acids.

Cyanogen Bromide: CNBr, and *Cyanogen Iodide*: CNI, are volatile crystalline solids, and are produced by treating mercuric cyanide or potassium cyanide with bromine or iodine respectively. Both possess a similar penetrating odour to that of the two chlorides. Cyanogen iodide is often contained in commercial iodine.

COAL-GAS.[1]

Coal gas is a complex mixture of various gases produced by the destructive or dry distillation of coal. The coal when distilled also yields a number of liquid and solid products, which are contained in *coal-tar*—a thick, oily, black liquid; and in the *ammoniacal-liquor*—an aqueous liquid, smelling strongly of ammonia and ammonium sulphide. The apparatus used in the manufacture of coal-gas consists of the retorts in which the coal is heated, the condensers for removing the coal-tar and ammoniacal-liquor, the purifiers for separating gaseous impurities, and gasometers for storing the gas.

The *retorts* are made of fire-clay, and so that their cross section has a ⌓-shape; they are closed at one end and are arranged in the furnace in a horizontal position, with their open ends projecting slightly outwards. After the charge of coal has been introduced, the open ends are closed by an iron plate, which can be bolted on, and from which a vertical iron tube passes upwards. This iron

[1] By the Editor.

tube, which conveys away all the products of distillation from the retorts, dips under the surface of water contained in a large iron tube running in a horizontal position above the retorts and called the *hydraulic main.* Most of the tar and much of the ammonia is here condensed, and when the liquid reaches a certain height it runs off through an opening into the *tar-well*—a large reservoir receiving all the liquid products of distillation. The gas next passes through a series of upright iron tubes, called *atmospheric condensers*, which are freely exposed to the air, and so cool the gas and condense a further quantity of liquid products. But in order to completely remove these substances, as well as some of the gaseous impurities, the gas is passed through the *scrubbers*, or tall vessels filled with fragments of coke, and kept continually moist by a descending spray of cold water. The gas enters at the base of the scrubber and escapes near the top. It now only remains to remove traces of gaseous impurities, especially sulphuretted hydrogen, carbon disulphide, and other sulphur compounds, which impart an unpleasant odour to the gas, and which, when burnt, produce sulphurous and sulphuric acids. This final purification is effected in the *purifiers*, which consist of large chambers containing thin layers of dry slaked-lime or of ferric hydrate on shelves. The lime then absorbs the sulphuretted hydrogen and other sulphur compounds, together with any carbonic acid which may be present, and is converted into *spent-lime*—a dirty-green amorphous mass of various compounds of calcium, with a very offensive odour. If ferric hydrate is employed it is converted by sulphuretted hydrogen into ferrous sulphide and free sulphur, and the former compound is partially oxidized on afterwards exposing the mass to the air. But when the quantity of free sulphur becomes large, the ferric hydrate can no longer effect the purification, and is then sent to the sulphuric acid works to burn out the sulphur and again obtain pure ferric oxide. Ferric hydrate does not remove carbonic acid, and it must be, therefore, mixed with a certain proportion of slaked-lime in order to get rid of this impurity. The presence of sulphuretted hydrogen in coal-gas may be detected by allowing a jet of the gas to play on a piece of paper impregnated with a solution of lead acetate. If the paper does not become blackened after a few seconds, the gas may be said to be free from this impurity. This test does not, however, detect the presence of carbon disulphide or other sulphur compounds.

The gases contained in coal-gas may be divided into three classes :—

(i.) *Diluents*, which have practically no illuminating power, but which are of special value when the gas is used for heating purposes. These consist of *hydrogen*, *marsh gas*, and *carbonic oxide*, and constitute from 85 to 90 per cent. by volume of the entire gas.

(ii.) *Illuminants*, to which the illuminating power of the gas is due, and which consist of hydrocarbons containing more carbon in their molecule than marsh gas. They are sometimes called *heavy hydrocarbons*. These illuminants are principally *ethylene* (C_2H_4), *propylene* (C_3H_6), *butylene* (C_4H_8), *acetylene* (C_2H_2), and *benzene* (C_6H_6).

(iii.) *Impurities*, which consist of *sulphuretted hydrogen*, *carbon disulphide* and other sulphur compounds, together with traces of *carbonic acid*, *oxygen*, and *nitrogen*, the two latter being derived from the air.

The composition of coal-gas depends upon the temperature at which the coal is distilled and upon the kind of coal used. The gas also varies in composition at different stages of the distillation. If the temperature is high, the heavy hydrocarbons are decomposed and a large volume of gas of low illuminating power is obtained. And if cannel coal is employed the gas contains a much larger proportion of these heavy hydrocarbons than that obtained from ordinary bituminous coal. The following table gives the composition of two samples of coal-gas. No. 1 is ordinary London gas, made from a mixture of bituminous coal and a small quantity of cannel ; No. 2 is gas made entirely from cannel coal and supplied to the Houses of Parliament :—

	No. 1.	No. 2.
Marsh Gas	35·89	41·87
Hydrogen	50·68	41·72
Carbonic Oxide	3·98	4·98
Heavy Hydrocarbons	4·08	8·72
Nitrogen	4·93	2·71
Oxygen	9·26	none
Carbonic Acid	0·18	none
	100·00	100·00

The greater part of the nitrogen which the coal contains is converted into ammonia during the distillation. An aqueous

solution of this ammonia constitutes the ammoniacal-liquor which collects in the tar-well. The ammonia is contained in this liquid partly in the free state, and partly in combination as ammonium carbonate, sulphide, cyanide, &c. This ammoniacal-liquor is now the chief source of ammonia and its compounds.

The coal-tar which is also found in the tar-well is a highly complex mixture of a large number of organic compounds. Among these may be mentioned the liquids—benzene and its homologues, aniline and phenol (carbolic acid); and among the solids—paraffin, napthalene, and anthracene. When the tar is distilled the more volatile liquids pass over and produce a combustible mixture of various compounds, called *coal-tar naphtha*. Coal-tar is used for a variety of purposes, some of which depend upon the antiseptic properties of the phenol which it contains, but by far the largest quantities are consumed in the manufacture of the beautiful coal-tar or aniline colours.

After the distillation is finished a considerable portion of the carbon present in the coal remains behind in the retorts as a grey porous mass, containing also the whole of the ash of the coal. This constitutes *coke*. At the same time, owing to the decomposition of some of the heavy hydrocarbons during distillation, a layer of extremely hard and compact carbon collects on the upper surface of the retorts. This form of carbon is called *gas-carbon*; it is used in the construction of some galvanic batteries and for highly refractory crucibles.

TITANIUM.

Chemical Symbol: Ti.—*Atomic Weight*: 48·2.

This element, which in many respects is closely allied to silicon, is also always found in nature, combined with oxygen.

Titanium dioxide or titanic anhydride: TiO_2, either free or combined with bases, is the form in which the element always occurs. Free titanic anhydride is found in three varieties: *rutile*, *anatase*, and *brookite*, which, although chemically the same, have different crystalline and other physical characteristics. Rutile crystallizes according to the tetragonal system, anatase and brookite according to the rhombic, and titanic anhydride is therefore trimorphous. Of the other naturally occurring compounds of titanium,

ilmenite or *titanic iron*, probably ferrous titanate, and *titanite* or *sphene*, calcium titanate and silicate, are the most important.

Free titanium is obtained in the following manner. Two iron boats, one containing dry potassium fluotitanate : K_2TiF_6, and the other metallic sodium, are brought into a tube of hard glass, which is then filled with *pure* hydrogen. The boat containing the fluotitanate is first heated to redness, then that containing the sodium, so that the vapour of the metal is carried by the hydrogen over the hot titanium salt. By this process sodium and potassium fluorides are produced and free titanium. If the two former compounds are afterwards extracted by hot water the titanium remains behind as a dark-grey amorphous powder, resembling iron which has been reduced in hydrogen. The element, in this pulverulent form, burns brilliantly when heated in oxygen or the air, forming titanic anhydride : TiO_2. It dissolves easily in hydrochloric acid, with evolution of hydrogen, probably producing a solution of titanium dichloride : $TiCl_2$. It burns when heated in chlorine, giving titanium tetrachloride : $TiCl_4$.

The material used for the preparation of titanium compounds is nearly always rutile. This substance, like quartz, is insoluble in hydrochloric acid, but may be brought into solution either by fusing with caustic potash or potassium carbonate, or with acid potassium sulphate, or, finally, by heating with concentrated sulphuric acid until the greater part of the liquid has been volatilized.

Titanic Anhydride : TiO_2.—The titanium sulphate produced by either of the last two methods dissolves in cold water, and from this solution titanic acid is precipitated in white flocculent masses on the addition of alkalies or alkaline carbonates, and is not redissolved by an excess of these substances. The dilute aqueous solution of titanium sulphate is decomposed on boiling, and deposits titanic acid as a white powder, which is only slightly soluble in concentrated sulphuric acid.

Potassium titanate, obtained by fusing powdered rutile with three times its weight of potassium carbonate, does not dissolve when the fused mass is afterwards treated with water, but forms acid potassium titanate, which is insoluble in water, and which can therefore be purified by washing. This acid salt dissolves, however, in cold hydrochloric acid, and when the solution is diluted with water and heated to boiling, titanic acid is precipitated as a white powder.

This form of titanic acid is scarcely soluble in water containing hydrochloric acid or ammonium chloride, but when washed with pure water passes in a milky state through the filter.

The titanic acid precipitated by boiling aqueous solutions containing hydrochloric or sulphuric acid always contains traces of the acid mixed with it, from which, however, it may be completely freed by digesting with ammonia, which has no action on the titanic acid.

The white precipitate produced by ammonia in a cold hydrochloric acid solution of titanic acid is said to have the composition : $Ti(OH)_4$. This compound is easily soluble in dilute acids, but is converted on warming into an acid containing less water—metatitanic acid, of the probable composition : $TiO(OH)_2$, which is only slightly soluble in acids. The titanic acid precipitated by boiling a sulphuric acid solution is insoluble in acids except concentrated sulphuric acid.

If metallic zinc is added to a hydrochloric acid solution of titanic acid, the nascent hydrogen which is produced reduces the titanic acid to the hydrated sesquioxide. In consequence of this reduction the liquid becomes of a violet-blue colour, and after a time, if the solution was not too dilute, a dark blue or violet blue precipitate separates out, which again becomes white when exposed to the air from absorption of oxygen.

Titanium Sesquioxide : Ti_2O_3, is obtained in the anhydrous state by glowing titanic anhydride in a stream of hydrogen. It is a black powder insoluble in nitric or hydrochloric acid, but dissolving in sulphuric acid to form a violet solution. When strongly glowed in the air it becomes white, being reconverted into titanic anhydride.

Titanium Tetrachloride : $TiCl_4$.—This compound, which closely resembles silicon tetrachloride, except that it is less volatile, is obtained, like silicon chloride, by heating an intimate mixture of rutile and charcoal in chlorine. It then distils over into a cooled receiver as a heavy liquid, usually with a yellowish tinge due to traces of ferric chloride. When purified by redistillation its specific gravity is 1·76, and boiling point 136°. It fumes strongly in moist air and has a vapour density of 6·8, corresponding to the molecular formula : $TiCl_4$. Water at once decomposes it, with considerable evolution of heat, into hydrochloric and titanic acids. Titanium chloride absorbs considerable quantities of ammonia,

yielding a reddish-brown powder of the composition : $TiCl_4, 4NH_3$, which is easily decomposed by moist air.

Titanium Tetrafluoride : TiF_4, is a colourless, fuming liquid, obtained by heating a mixture of titanic anhydride and fluor-spar with concentrated sulphuric acid.

Fluotitanic Acid : H_2TiF_6, which is analogous in composition to fluosilicic acid, is obtained by dissolving titanic acid in hydrofluoric acid. If the aqueous solution is neutralized with potassium carbonate, or if potassium titanate is dissolved in hydrofluoric acid, or, finally, if rutile is fused with acid potassium fluoride, potassium fluotitanate : K_2TiF_6, is easily obtained in the crystalline form.

Titanium belongs to those elements which unite with nitrogen to form compounds stable at a red heat. If titanium chloride is saturated with dry ammonia, and the resulting solid : $TiCl_4$, $4NH_3$ heated to redness in gaseous ammonia, *titanium nitride* : Ti_3N_4, remains behind as a copper-coloured mass, with metallic lustre, and which evolves ammonia when fused with solid caustic potash.

In the slag from blast furnaces, where iron ores containing titanium have been used, bright-red, lustrous crystals in cubes are often found, and sometimes in considerable quantities. They consist of a chemical compound of titanium nitride and cyanide.

MOLYBDENUM.

Chemical Symbol : Mo.—*Atomic Weight* : 96.

Molybdenum occurs chiefly in nature as *molybdenite*, the disulphide : MoS_2, and more rarely as *wulfenite*, lead molybdate : $MoO_2 \cdot O_2Pb$. Molybdenite, which closely resembles graphite in its appearance, is a soft mineral, feeling greasy to the touch, and easily marking paper. It is, however, heavier than graphite, and is further distinguished by giving an olive-green streak on porcelain, instead of a grey one like graphite.

Molybdenum is readily obtained by heating one of its chlorides or oxides in hydrogen, when the walls of the glass tube used for the reduction often become covered with a brilliant, metallic-like mirror of the free substance. In its physical properties, molybdenum far more closely resembles the metals than the non-metals.

It is of a silver-white colour, with a strong metallic lustre, very hard, melts with extreme difficulty, and is possibly infusible when quite pure. Its specific gravity is 8·6. In the air it remains unchanged, and only combines with oxygen when heated to low redness. Hydrochloric acid or dilute sulphuric acid has no action on it. Concentrated sulphuric acid converts it into a brown mass. Aqua regia easily dissolves it, and nitric acid converts it into one of the oxides.

For the preparation of molybdenum compounds from molybdenite, the mineral is powdered, and placed in an open, inclined crucible, which is then surrounded with pieces of glowing charcoal and heated to low redness, with frequent stirring, as long as sulphurous anhydride is evolved. Crude and impure molybdic anhydride then remains behind as a yellow powder. This compound is insoluble in water, but dissolves in aqueous ammonia, leaving the impurities and the unoxidized molybdenite behind. A further quantity of molybdenum may generally be obtained from the residue by roasting again as before. On evaporating down the ammoniacal solution ammonium molybdate crystallizes out, and from a solution of this salt, cautious addition of dilute hydrochloric or nitric acid precipitates molybdic acid as a white powder, scarcely soluble in water, but easily soluble in an excess of acid.

Molybdenum forms several compounds with oxygen. We distinguish, for example, *molybdenum sesquioxide*: Mo_2O_3, obtained by reduction from molybdic anhydride as a black powder insoluble in acids, also *molybdenum dioxide*: MoO_2, which remains behind as a red crystalline mass when ammonium molybdate is heated in a closed crucible, and

Molybdic Anhydride: MoO_3, the best known oxide. Molybdic anhydride or molybdenum trioxide remains as delicate white crystals, yellowish when hot, on heating ammonium molybdate in an open crucible. It melts at a red heat, and sublimes in small, thin, glistening scales. Acids do not dissolve it, but with alkalies it forms soluble crystalline compounds—the molybdates.

Molybdic Acid: $MoO_2(OH)_2$, is a dibasic acid, and separates from a solution of any of its salts on careful addition of dilute hydrochloric acid as a white crystalline powder, easily soluble in excess of acid. If zinc is added to a hydrochloric acid solution of molybdic acid, a blue colour is first produced which soon becomes

green, and finally dark-brown. These changes in colour are due to the reduction of the molybdic acid by the nascent hydrogen.

Among the salts of molybdic acid that of ammonium is of considerable importance in analytical chemistry; it is used for the detection and estimation of phosphoric acid in acid liquids containing other compounds. If such a liquid containing phosphoric acid—for example, the aqueous or acid extract of a soil or manure—is mixed with an excess of a solution of ammonium molybdate strongly acidified with nitric acid and then warmed, a yellow crystalline precipitate of the composition: $11MoO_3, PO(ONH_4)_3, 6H_2O$, and containing the whole of the phosphoric acid, is thrown down. This precipitate is insoluble in water or dilute acids, but easily soluble in ammonia. If this yellow compound is boiled with aqua regia, the ammonia is destroyed, and on allowing the solution to evaporate at the ordinary temperature, *phosphomolybdic acid*: $11MoO_3, PO(OH)_3, 12H_2O$, crystallizes out in yellow prisms. The acid is easily soluble in water, and produces, with acid solutions of ammonium salts or nitrogenous organic bases, yellow compounds which are insoluble in dilute acids.

Ammonium molybdate, when mixed with an acid solution of arsenic acid or an arsenate, produces a similar yellow insoluble salt.

Several chlorides of molybdenum are known as: $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$; besides these, two oxychlorides of hexad molybdenum also exist, viz.: $MoOCl_4$ and MoO_2Cl_2.

TUNGSTEN.

Chemical Symbol: W.—*Atomic Weight*: 184.

This element resembles molybdenum in many respects, but is distinguished from it by the high specific gravity of the free element and of its compounds.

Tungsten never occurs free in nature, and its compounds are only found in small quantities. The best known of the tungsten minerals are *wolfram* (ferrous and manganous tungstate) and *scheelite* (calcium tungstate), the former of a dark grey colour with a specific gravity of 7·5, the latter consisting of white crystals also remarkable for its high specific gravity.

Tungsten, prepared by the reduction of tungstic anhydride in a stream of hydrogen at a bright red heat, forms small grey crystalline particles, which under the burnisher become lustrous like iron. Its specific gravity is about 19, and thus nearly approaches that of gold. It is only difficultly fusible, especially in large quantities, is brittle, and so hard that it scratches glass. At the ordinary temperature it remains unchanged in the air; but when it is heated in the pulverulent form it burns easily, and produces tungstic anhydride. Hot nitric acid oxidizes it to the same product.

Of the oxides of tungsten, the dioxide, WO_2, is known as a brown powder insoluble in hydrochloric or nitric acid. More important than this is the trioxide—

Tungstic Anhydride: WO_3, which remains behind as a yellow powder, insoluble in water and acids, when powdered wolfram is heated with nitric acid, while the iron and manganese go into solution. It may also be obtained by acting on scheelite with nitric or hydrochloric acid. This yellow tungstic anhydride dissolves readily in alkalies (including ammonia), forming soluble crystalline salts—the *tungstates*. From a cold solution of these salts dilute acids precipitate white *tungstic acid* of the composition: $WO(OH)_4$, which, when dried over sulphuric acid, passes into the dibasic acid: $WO_2(OH)_2$, and when heated to the boiling point of water is converted into yellow tungstic anhydride.

If tungstic acid is precipitated from a solution of a tungstate by hydrochloric acid, and then a piece of zinc added to the acid liquid, a beautiful dark blue colour is produced, due to a soluble oxide of uncertain composition, and which, when exposed to the air, again oxidizes to tungstic acid.

The normal tungstates are salts of the dibasic acid: $WO_2(OH)_2$. Others, however, possess a more complex composition; for example, the metatungstates of which the sodium salt has the formula: $Na_2W_4O_{13} + 10H_2O$. The common sodium tungstate of commerce is still more complex, and has the composition: $Na_{10}W_{12}O_{41}$.

Corresponding to phosphomolybdic acid is a *phosphotungstic acid* of similar composition. And a remarkable double compound of tungstic and silicic acids is known—*silicotungstic acid*, the soluble and crystalline compounds of which are obtained by boiling acid alkaline tungstates with gelatinous silicic acid.

Like molybdenum, tungsten unites in several proportions with

chlorine. The hexachloride: WCl_6, corresponding to tungstic anhydride, forms a dark violet mass, melting at 275° to a red liquid, and boiling at 346°. It is decomposed by water into tungstic and hydrochloric acids. This compound may be obtained by moderately heating free tungsten in a stream of pure chlorine. Chlorides of composition: WCl_5, WCl_4, WCl_2, are also known. Corresponding to tungsten hexachloride are two oxychlorides: $WOCl_4$ and WO_2Cl_2, both solid crystalline substances.

Tungsten, when alloyed, in small quantities, with iron, increases its hardness; steel containing about 5 per cent. of tungsten—known as *tungsten-steel*—is distinguished by its great hardness.

VANADIUM.

Chemical Symbol: V.—*Atomic Weight*: 51·3.

Vanadium belongs to the rarer elements, although it is widely distributed in minute quantities; it occurs especially in certain ores of iron. Vanadic acid is usually prepared from these iron ores, the mineral *vanadinite*—lead vanadate—being too rare to serve for the preparation of vanadium compounds. Considerable quantities of vanadium compounds are now obtained in England from a mineral called *mottramite*, a double vanadate of lead and copper, occurring in Lancashire.

Vanadium, obtained by glowing the dichloride in pure hydrogen, is a grey powder of specific gravity 5·5, which remains unchanged in the air, and can be raised to redness out of contact with air without melting, but when heated in the air burns to form vanadic anhydride. It also unites readily with nitrogen at a red heat. It is insoluble in hydrochloric acid, but dissolves easily in nitric acid to a blue solution. Fused with caustic soda, hydrogen is evolved, and sodium vanadate produced.

Of the oxides of vanadium the best known is:—

Vanadic Anhydride: V_2O_5, analogous in composition to phosphoric anhydride, and, like this, forming an acid, but little known in the free state, which is tribasic. Vanadic anhydride, obtained by gently roasting ammonium vanadate, is a reddish powder, which melts when heated to redness, and crystallizes on cooling. It is slightly soluble in water, giving a solution of a yellow colour, but

dissolves easily in acids or alkalies, forming with the latter soluble crystalline vanadates.

Metallic zinc brought into contact with a hydrochloric acid solution of vanadic acid produces first a blue colour, which afterwards changes to green.

The extraction of vanadic anhydride from iron ores containing vanadium may be carried out in the following manner. The ores are finely powdered, mixed with nitre and heated. The mass, which contains potassium vanadate, is then extracted with water, nearly neutralized with nitric acid and then precipitated with barium chloride. Insoluble barium vanadate is thus produced, which is washed with water, and then decomposed by boiling with sulphuric acid. The acid liquid is then separated from the barium sulphate, neutralized with ammonia, concentrated, and solid pieces of ammonia chloride added, when ammonium vanadate, which is soluble in water, but insoluble in ammonium chloride, gradually separates out. This salt, when washed with ammonium chloride solution, dried and gently heated in an open crucible, leaves vanadic anhydride behind.

NIOBIUM AND TANTALUM.

These rare elements are but little known either in the free state or in combination with other substances. Their compounds are most nearly related to those of vanadium. They both form anhydrides, corresponding to vanadic anhydride, and having therefore the composition: Nb_2O_5 niobic anhydride and Ta_2O_5 tantalic anhydride, in which the elements are pentads.

Niobium and tantalum nearly always occur associated with one another in nature; they are found in the minerals *columbite* and *tantalite*, which are essentially ferrous niobate and tantalate, in *samarskite*, a niobate and tantalate of the metals of the yttrium and cerium groups, and in some other still rarer minerals, from which the oxides are best extracted by fusion with acid potassium sulphate.

Niobic and tantalic anhydrides are white powders, yellow when hot, and insoluble in water, acids, or alkalies. They are principally distinguished from one another by their very different specific gravity.

THE METALS.

THE classification of the elements into the two great divisions, metals and non-metals, dates from a time when a number of physical properties were ascribed to the metals, which were thought to be peculiar to them and which were considered suitable for their distinction from the non-metals. Such characteristic and peculiar properties of the metals were, for example, their lustre (whence the term 'metallic lustre'), their conductivity for heat and electricity, a high specific gravity (exceeding 6), opacity to light, and others.

We now know that not one of these physical characteristics belongs exclusively to the metals. Iodine, tellurium, and graphite possess metallic lustre. Tellurium conducts heat, and graphite, as well as selenium (in a less degree) conduct electricity. On the other hand, metals are known—*e.g.* potassium and sodium—of which the specific gravity is not only less than 6, but which are even lighter than water.

The exact meaning, therefore, of the words *metal* and *non-metal* cannot be sharply defined—it is impossible to say what properties are exclusively peculiar to the former and what to the latter, just as it is impossible to exactly classify any series of natural substances.

This, however, by no means prevents us from grouping together, according to artificial rules, certain classes of natural phenomena and substances which possess some similarity with one another; and by so doing we not only obtain a clearer conception of the entire subject, but also make it easier for the student.

It cannot be denied that a more comprehensive view of the more than sixty elements known to modern chemistry is obtained if we classify those resembling one another into certain groups. This has already been done with the elements of the sulphur and nitrogen groups, and with the halogens. For the same reason, it is therefore advisable to retain the division of the whole of the elements into non-metals and metals; and since the application of

certain physical properties for a sharp classification has proved useless, we must seek for other peculiarities which shall serve to separate oxygen, hydrogen, carbon, the halogens, the members of the sulphur and nitrogen groups, &c., from potassium, aluminium, zinc, lead, silver, &c., when writing or speaking of chemical facts.

An artificial classification of the elements cannot be obtained from their *physical* properties, and we must therefore base our divisions on their *chemical* behaviour. For this purpose we can use the chemical character of their compounds with oxygen.

The larger number of the elements when united with oxygen produce oxides of a basic character, the other elements produce almost exclusively oxides with acid properties. To the latter class belong those elements which we have as yet discussed, and which are called non-metals. *Those elements of which the oxides usually possess basic properties are the* metals.

That this division of the elements into non-metals and metals is an artificial and not a natural classification, and that it cannot therefore be consistently carried out, is proved by the following considerations:—(i.) Oxygen belongs to neither class; but is reckoned with the non-metals. (ii.) Hydrogen often plays the part of a metal, and its oxide, water, behaves sometimes as a base and sometimes as an acid. (iii.) Antimony, although included under the non-metals, forms a basic oxide with oxygen—antimonous oxide. (iv.) The metals manganese and chromium form oxides of acid properties—manganic and chromic anhydrides—as well as others of basic properties. (v.) The basic oxides of many metals—*e.g.* lead oxide, zinc oxide—play the part of acids in some compounds. Lead oxide, which combines with nitric acid to form lead nitrate, also unites with potash and forms a salt—potassium plumbite. In the former compound it plays the part of a base, in the latter that of an acid.

It is clear, therefore, that the division of the elements accordingly as they produce acid or basic oxides, like every other artificial classification, cannot be carried out in every particular; it is only suited to separate certain elements which differ from one another in certain important particulars.

The Chemical Constitution of Salts.

With the definition of a metal is connected that of a salt, since all salts of inorganic chemistry (if we consider ammonium as a

metal) are metallic compounds; and a short, accurate definition of a *salt* is scarcely easier than that of a *metal*.

On p. 78 it has been stated that salts are produced by the union of acids with bases, which tells us how they are produced, but not of what they actually consist.

Salts are binary compounds consisting of an electro-positive constituent—*e.g.* a metal, and an electro-negative[1] constituent—*e.g.* a halogen or acid radical. They are usually decomposed by electrolysis into these two constituents—the former separating at the negative, the latter at the positive pole. Common salt (sodium chloride) when fused or dissolved in water is decomposed by an electric current into chlorine and sodium, of which the former goes to the positive pole and the latter to the negative. If water is present it is decomposed by the sodium, so that instead of sodium we obtain hydrogen and sodium hydrate at the negative pole.

Salts of this kind contain a metal in *direct* union with a negative element, the halogen. They are called *haloid-salts* because only the halogens and the compound substances resembling them, cyanogen, sulphocyanogen, &c., but not the other non-metals, can thus unite directly with the metals to form salts.

Another class of salts, called *amphid-salts*, consist also of an electro-positive and electro-negative constituent, which, however, are not directly united with one another, but are combined through the intervention of one or more atoms of oxygen or sulphur. If the uniting element is oxygen, the compound is called an *oxysalt*, if sulphur a *sulphosalt*.

A haloid-salt may be converted into an oxysalt by the introduction of an atom of oxygen—for example, in the conversion of sodium chloride into sodium hypochlorite: $NaCl + O = NaOCl$, in which the sodium and chlorine are not now directly united with one another, but through the atom of oxygen, common to both.

The negative portion, and sometimes the positive portion also, of the oxysalts usually consists of a compound radical. Thus, potassium nitrate: $NO_2 \cdot OK$, contains the monad radical nitric peroxide (nitryl): NO_2, sodium sulphate: $SO_2\begin{cases} ONa \\ ONa \end{cases}$ contains the diad radical sulphurous anhydride (sulphuryl): SO_2, and sodium

[1] Using the obsolete but convenient nomenclature of the electro-chemical theory.—ED.

phosphate : $PO\left\{\begin{matrix}ONa\\ONa\\ONa\end{matrix}\right.$ the triad radical : PO, which has not yet been isolated. And these three acid radicals are all united to their respective metals—the positive portion of the salt, by one, two, or three atoms of oxygen respectively.[1] Two metals may also be united with one another by oxygen, as in potassium plumbite : $Pb\left\{\begin{matrix}OK\\OK\end{matrix}\right.$ in which the lead is the negative element, and the potassium the positive.

As an example of the sulphosalts may be mentioned the compound produced by the combination of carbon disulphide with potassium sulphide, potassium sulphocarbonate : $CS\left\{\begin{matrix}SK\\SK\end{matrix}\right.$ corresponding to ordinary potassium carbonate : $CO\left\{\begin{matrix}OK\\OK\end{matrix}\right.$ in which compounds the respective oxygen and sulphur atoms may displace one another. For although a compound of the composition: $CO\left\{\begin{matrix}OK\\SK\end{matrix}\right.$ is at present unknown, the previously described (p. 168) sodium thiosulphate : $SO_2\left\{\begin{matrix}ONa\\SNa\end{matrix}\right.$ is an example of these little known inorganic compounds. In organic chemistry they are much more numerously represented.

We also distinguish salts called *normal*, *acid*, and *basic* salts. Monobasic acids—*i.e.* those containing only one atom of hydrogen displaceable by one atom of a monad metal, *e.g.* nitric acid : $NO_2{\cdot}OH$—can only form normal salts with monacid bases—*i.e.* those containing only one atom of hydrogen displaceable by an acid radical, *e.g.* caustic potash : KOH.

Acid salts can only be produced from polybasic acids—*i.e.* those which contain more than one atom of displaceable hydrogen, as sulphuric or phosphoric acid, when a portion of their hydrogen is displaced by a metal (comp. p. 56). In the same manner, basic salts are formed from polyacid bases—*e.g.* lead hydrate : $Pb\left\{\begin{matrix}OH\\OH\end{matrix}\right.$ and ferric hydrate : $Fe\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$ when a portion only of their hydro-

[1] The electrolysis of such an oxysalt has already been explained (p. 79).—ED.

gen is displaced by an acid radical or by a haloid. The following are some examples of basic salts :—

Basic lead nitrate	$Pb\begin{cases} O{\cdot}NO_2 \\ OH \end{cases}$
Basic lead chloride	$Pb\begin{cases} Cl \\ OH \end{cases}$
Basic ferric nitrate	$Fe\begin{cases} ONO_2 \\ OH \\ OH \end{cases}$
Basic ferric sulphate	$Fe\begin{cases} O_2SO_2 \\ OH \end{cases}$
Basic ferric chloride	$Fe\begin{cases} Cl_2 \\ OH \end{cases}$

Many compounds which are called basic compounds, but which do not contain the acid radical or haloid and the metal in equivalent proportions, are best considered as mixtures of a normal salt and a metallic hydrate. Thus the basic antimonous chloride, referred to on p. 257, and sometimes represented by the formula : $Sb\begin{cases} O \\ Cl \end{cases}$ contains varying quantities of oxygen and chlorine united with the same quantity of antimony, and is, therefore, better considered as a mixture of antimonous chloride : $SbCl_3$, and antimonous oxide : Sb_2O_3.

A triacid base—*e.g.* aluminium hydrate : $Al\begin{cases} OH \\ OH \\ OH \end{cases}$ requires three molecules of monobasic acid in order to produce a normal salt, while at the same time three molecules of water are also produced : $Al(OH)_3 + 3NO_2OH = AlO_3(NO_2)_3 + 3H_2O$; and in the same way a molecule of the same base will require only one molecule of a tribasic acid : $Al(OH)_3 + PO(OH)_3 = AlO_3{\cdot}PO + 3H_2O$. If, however, we have a dibasic acid united to the same triacid base, we shall require three molecules of the former to two of the latter. Thus, normal aluminium sulphate is produced in this way :—

$$2Al(OH)_3 \quad + \quad 3SO_2(OH)_2 \quad = \quad Al_2O_6(SO_2)_3 \quad + \quad 6H_2O.$$

Normal salts may also be produced by the union of two molecules of a dibasic acid with one of a triacid, and one of a monacid

base. Common alum: $\left.\begin{matrix}AlO_3\\KO\end{matrix}\right\}2SO_2$, for example, is a normal sulphate of the two metals aluminium and potassium, and is thus formed:—

$$Al(OH)_3 + KOH + 2SO_2(OH)_2 = \left.\begin{matrix}AlO_3\\KO\end{matrix}\right\}2SO_2 + 4H_2O.$$

From these examples it will be seen that a salt may be defined either as an acid in which the hydrogen is displaced by a metal, *or* as a base in which its hydrogen is displaced by an acid radical, or its hydroxyl by a haloid element or some similar group of elements.

The normal salts often have no action on vegetable colours—*i.e.* are said to be neutral, and hence this class of salts is sometimes called neutral salts. But some normal salts have a strong alkaline or acid reaction, and even some acid salts react occasionally alkaline, while, on the other hand, some acid salts possess a neutral reaction. Red litmus paper is strongly blued by normal potassium carbonate: $CO\left\{\begin{matrix}OK\\OK\end{matrix}\right.$ and by normal potassium phosphate: $PO\left\{\begin{matrix}OK\\OK\\OK\end{matrix}\right.$ and even faintly by monacid potassium phosphate: $PO\left\{\begin{matrix}OK\\OK\\OH\end{matrix}\right.$ On the other hand, acid sodium carbonate: $CO\left\{\begin{matrix}ONa\\OH\end{matrix}\right.$ reacts neutral. The cause of this is that the strongly basic properties of potassium hydrate are not neutralized by the weak carbonic acid, and that phosphoric acid, although one of the strongest acids, does not completely neutralize the potash in the monacid phosphate. (See App.)

Double Salts.—Compounds in which the chemical affinities of the combining atoms are completely satisfied are called *saturated compounds.* Such, for example, are potassium chloride: KCl, and platinum tetrachloride: $PtCl_4$. And it might be thought that these two compounds could not be capable of any further combination. But in spite of this they both unite to form a double, and very stable salt of the composition: $2KCl,PtCl_4$. And a large number of other similar double salts are also known.

In most of these cases where perfectly saturated compounds can unite with one another chemically and form new compounds, we are unacquainted with the forces which cause this union. Such compounds have been called *molecular compounds*—*i.e.* compounds

produced by the chemical union of molecules. This expression, of course, explains nothing, but simply states that the molecules of saturated compounds are capable of uniting with one another to produce new compounds.

The constitution of the haloid double salts may be expressed in the following manner. From a consideration of the composition of numerous double fluorides, it appears that two atoms of monad fluorine can coalesce to form what plays the part of a diad atom. Thus in the compound *KF, HF* (comp. p. 136), we can consider that the two monad atoms of fluorine unite to form one diad atom of double the atomic weight, which may be indicated by the symbol $\bar{\mathrm{F}}$. This double compound then becomes $\mathrm{K\bar{F}H}$, analogous to KOH. Just in the same manner the double chloride of potassium and platinum, which may be written: $2KCl,(PtCl_2)Cl_2$, may be considered as two atoms of potassium united with the diad radical $PtCl_2$ by the other four atoms of monad chlorine, which have coalesced to form two diad atoms, thus :—

$$\mathrm{K_2Cl_2, (PtCl_2)Cl_2} = \left.\begin{matrix}\mathrm{K\bar{Cl}}\\ \mathrm{K\bar{Cl}}\end{matrix}\right\}\mathrm{PtCl_2}.$$

In the same manner the double iodide of potassium and mercury: $2KI, HgI_2$ may be written: $\left.\begin{matrix}\mathrm{K\bar{I}}\\ \mathrm{K\bar{I}}\end{matrix}\right\}\mathrm{Hg}$, and the double cyanide of potassium and silver, $\mathrm{K\bar{Cy}Ag}$. The constitution of the potassium ferrocyanides, as well as other similar compounds, may be interpreted in the same way.

The oxysalts also unite together to form double salts. Zinc sulphate, for example, unites with potassium sulphate to form the compound : $SO_2O_2Zn + SO_2(OK)_2 + 6H_2O$, which is produced from zinc sulphate by the substitution of a molecule of water of constitution, by potassium sulphate.

SPECTRUM ANALYSIS.

It has been previously mentioned (p. 308), that a non-luminous flame becomes luminous when a solid body is raised to incandescence in it, and then emits white light. But if metallic compounds are introduced into such a flame and there volatilize, for which the metallic chlorides are best adapted, the heated vapour of the metal imparts a colour to the flame, peculiar to each. Thus

compounds of sodium colour the flame an intense yellow, those of potassium violet, and those of lithium crimson. But owing to the similarity of many of these colours when viewed by the naked eye, they are not always suitable for directly determining which metal may or may not be present. It is often difficult to say by mere observation whether a given flame is coloured red by strontium or calcium, or whether a flame coloured yellow by sodium, also contains potassium, since the bright yellow sodium flame can completely mask the violet colour due to potassium compounds, even when the latter substance is present in considerable quantities.

But something quite different is observed if, instead of simply looking at a flame with the naked eye, we allow the light to fall through a narrow slit on to a triangular prism of glass and then magnify the bent rays of light by a telescope. Light of different colours in passing through the prism is differently bent, and ordinary white light gives a band of colours extending from red to violet—a so-called continuous spectrum. The light from a glowing gas is broken up into its constituent parts in the same way: the spectrum in this case will not, however, be a continuous one, but will consist of bright lines separated by more or less dark spaces. And these bright lines always appear in those parts of the spectrum to which they belong; thus the red lines will always be in the red, the blue in the blue portion, and so on—each gaseous element having its own peculiar spectrum.

The coloured table of spectra forming the frontispiece shows firstly the continuous spectrum of sunlight and then the spectra of ten metals, which differ much from one another, both with regard to the number and to the position of their lines. Sodium, lithium, thallium, and indium possess at the most two lines each, while cæsium, rubidium, strontium, calcium, and barium have much more complex spectra. Cæsium, strontium, and indium have all blue lines, but their position, when compared with the same scale, is different. As is shown in the table, the blue strontium line is most to the left, then follow the two blue lines of cæsium more to the right, and still further to the right is the blue indium line.

A substance which is supposed to contain thallium, and which like thallium gives a green line but in a different position—either more to the right or to the left—certainly does not contain this metal. Such an observation would rather point to the existence of a new (hitherto unknown) element; for, as previously remarked, the position of the bright lines in the spectrum of any one element

is always the same under all conditions. In this way the new metals, rubidium, cæsium, thallium, indium, and gallium, have been discovered by the aid of spectrum analysis, and it is extremely probable that others will be added to this list. And although, as previously intimated, potassium compounds, even when present in considerable quantity, cannot be recognized by the naked eye in a flame in which sodium is volatilized at the same time, if we allow the light to fall through a slit and decompose it by the prism, the lines of both metals are easily seen in the spectrum.

The apparatus for spectrum analysis—called a spectroscope—as devised by Bunsen and Kirchhoff, to whom this delicate method

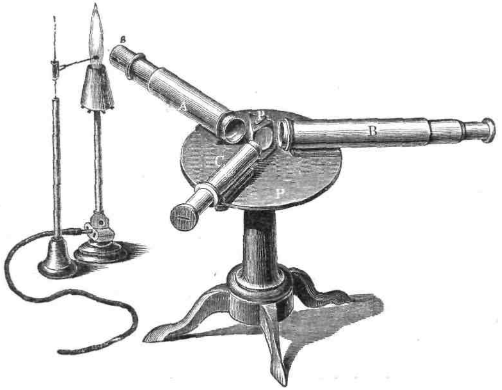


Fig. 58.

of chemical analysis is due, is shown in one of its simplest forms in fig. 58. On an iron stand are fastened three brass tubes, and between these is placed the glass prism. At the outside end of the tube A is a narrow slit, which can be widened or contracted at will, and through which the light from the heated substance passes on to the glass prism; the spectrum so produced is then observed through the telescope B. The third tube, C, contains a small reduced photographic scale, illuminated by a small gas flame

placed in front of it, and an image of which is thus reflected from one face of the prism into the telescope B. This serves to fix the position of any line in a given spectrum. All extraneous light must, of course, be excluded from the prism by covering it with a blackened box or cloth.

A little practice with the spectroscope soon enables one to determine the presence or absence of any metal in a given substance.

Those metals which are only volatilized with difficulty (*e.g.* iron), and which therefore do not become gaseous in the gas flame, are investigated by allowing powerful electric sparks to pass between poles of the metal, or between small carbon poles saturated with a solution of its chloride. Gases yield spectra in the same way. Hydrogen, when heated by the passage of electric sparks, appears bright red, and its spectrum consists essentially of a bright red, a green, and a blue line.

The results of spectrum analysis have also made it possible to determine the composition of the sun and other fixed stars. And in no heavenly body has an element been discovered which is unknown on the earth.

The great delicacy of spectrum analysis makes it especially valuable for chemical purposes. Most minute quantities of various metals, which it was previously quite impossible to detect, can be recognized with the greatest certainty by spectrum analysis. It has been calculated from experiments that one hundred-thousandth part of a milligramme of lithium chloride, and even one three-millionth part of a milligramme of sodium chloride may be easily detected by their spectra.

CLASSIFICATION OF THE METALS.

(*Compare with note in the Appendix on 'The Periodic Law.'*)

It has been repeatedly attempted to discover some physical or chemical properties of the metals which might serve to classify them into a series of divisions and sub-divisions. But, however desirable such a classification may be in simplifying the study of this large group of elements, all such attempts have only strengthened the conviction that the metals cannot be exactly divided upon any natural system into a number of distinct classes, and that, if such a classification is made, it must be according to some

artificial rules. The properties of the oxides and sulphides of the metals may serve as the basis of such an artificial classification.

One class of the metals forms oxides, or rather hydrates, which are easily soluble in water, the solutions of which have a powerful alkaline reaction; these hydrates are called the alkalies, and the corresponding metals the *metals of the alkalies.* The following five metals belong to this class—viz. *potassium*, *sodium*, *lithium*, *rubidium*, and *cæsium*, and the hypothetical compound metal *ammonium.*

A second class also yields soluble oxides, though far less soluble than the alkalies. These oxides also react faintly alkaline, but are at the same time allied to the oxides of the next—the so-called *earths*—and their corresponding metals are therefore called the *metals of the alkaline earths.* In this class the metals *calcium*, *strontium*, *barium*, *magnesium*, and *beryllium* are included. The two last-named metals, of which the oxides are only very slightly soluble in water, form connecting links with the next group.

The third group, of which the oxides are completely insoluble in water, and are called earths, are the *metals of the earths.* The chief representative of this group is *aluminium*, with which are associated the rarer metals, *indium*, *gallium*, *yttrium*, *erbium*, *cerium*, *lanthanum*, *didymium*, and *zirconium*, as well as some still rarer elements. The sulphides of this group (except indium) are not produced on the addition of sulphuretted hydrogen or an alkaline sulphide to a solution of one of their salts. The precipitate produced on adding sodium sulphide or ammonium sulphide to their solutions usually consists of the insoluble hydrate, while sulphuretted hydrogen is given off; chromic compounds when treated in this manner behave like the aluminium salts :—

$$Al_2Cl_6 + 3Na_2S + 6H_2O = 2Al(OH)_3 + 6NaCl + 3H_2S.$$

A fourth class includes those metals of which the sulphides are insoluble in water, but mostly soluble in dilute acids. These compounds are precipitated on adding an alkaline sulphide, such as ammonium sulphide, to a solution of one of their salts. They are not, however, produced when sulphuretted hydrogen is led through an acid solution of their salts. The metals of this group are: *iron*, *manganese*, *chromium*, *uranium*, *cobalt*, *nickel*, and *zinc.*

The fifth group includes those metals of which the sulphides are insoluble both in water and in dilute acids, and are therefore precipitated when sulphuretted hydrogen is led through an acid

solution. They are: *lead*, *thallium*, *bismuth*, *cadmium*, *tin*, and *copper*.

The metals belonging to the fourth and fifth groups are sometimes called the *heavy metals*.

The heaviest or so-called *noble metals* are: *mercury*, *silver*, *gold*, *platinum*, *iridium*, *palladium*, *rhodium*, *ruthenium*, and *osmium*. The sulphides of this group are also insoluble in dilute acids.

We now proceed to the discussion of the metals arranged in these six classes.

The Metals of the Alkalies.

At the commencement of this century it was universally believed that every metal must possess a comparatively high specific gravity—*i.e.* be considerably heavier than water (see p. 331). But when the metals of the alkalies were discovered by Davy this opinion was shown to be incorrect. Potassium and sodium are lighter than water, and lithium, which was discovered later, is only about one-half as heavy.

The metals of the alkalies are characterized by their strong chemical affinities for negative elements, and are therefore well adapted for withdrawing oxygen, sulphur, chlorine, &c., from combination with other elements. They belong to our most powerful reducing agents. Water is decomposed by them even at the ordinary temperature of the air. Their oxides and sulphides are easily soluble in water and are powerful bases. With the halogens they produce, like most other metals, neutral compounds, all of which are soluble in water.

POTASSIUM.

Chemical Symbol: K.—*Atomic Weight*: 39·1.

The strong attraction of the metals of the alkalies, and especially of potassium, for oxygen, makes it impossible for them to occur in the free state in nature. Potassium is chiefly found in the mineral kingdom in combination with oxygen and silica as a silicate, and in this form is a constituent of potash felspar; it also occurs, united with chlorine, as potassium chloride. The upper layer of the salt deposits at Stassfurth in Germany consists principally of

potassium chloride, which is largely used for the manufacture of other potassium compounds.

Potash felspar (orthoclase), which may be considered as a double compound of aluminium silicate and potassium silicate, and which is one of the constituents of granite, gradually becomes disintegrated under the influence of frost, and is then decomposed by water containing carbonic acid into insoluble aluminium silicate (clay) and soluble potassium silicate, or carbonate, which fertilizes the soil.

Nearly all land plants require potassium compounds for their growth and even for their existence, just as we require salt in our food. These potassium compounds are absorbed by their roots and converted in their structure into potassium salts of organic acids. And when the plants are burnt nearly the whole of the potassium which they contain remains behind as potassium carbonate or potash. This was formerly the material from which potassium compounds were almost exclusively prepared.

Potassium is a silver-white metal with a bright lustre. Its specific gravity is 0·87, it melts at 62°, and can be distilled at a red heat in a stream of hydrogen, giving a vapour of a bright green colour. At the ordinary temperature the metal is soft and can be easily moulded or cut with a knife, but at 0° it is hard and brittle. In consequence of its strong attraction for oxygen, the freshly-cut surface is only lustrous for a moment, and immediately afterwards becomes covered with a thin layer of oxide of a bluish colour. The white lustrous surface can only be preserved by melting the metal in a glass tube filled with hydrogen, then exhausting the gas, sealing up hermetically, and allowing the liquid metal to spread over the tube. When slowly cooled, the metal can sometimes be obtained in the crystalline form.

Potassium is now never prepared by the process by which Davy first obtained it—the decomposition of fused caustic potash by an electric current—as this only yields a very small quantity at one time. It is far better to reduce potassium carbonate with charcoal at a red-heat. The chemist is no longer compelled to prepare his own potassium, as it is now manufactured in chemical works at a far cheaper rate than it can be prepared in small quantities. Nevertheless, potassium is still an expensive substance, principally because it is only used in small quantities in the arts. Its price is about 6*s*. per ounce.

To obtain a good yield of potassium from potassium carbonate

and carbon, it is very necessary that the two substances should be mixed together as intimately as possible. And as this can scarcely be done by mechanical means, it is better to employ some organic salt of potassium rich in carbon, of which purified tartar, acid potassium tartrate, is the most suitable. The salt is heated in a covered crucible, first gently and then to redness, and the carbonaceous residue, consisting of an intimate mixture of potassium carbonate and charcoal, is then introduced into an iron retort. The

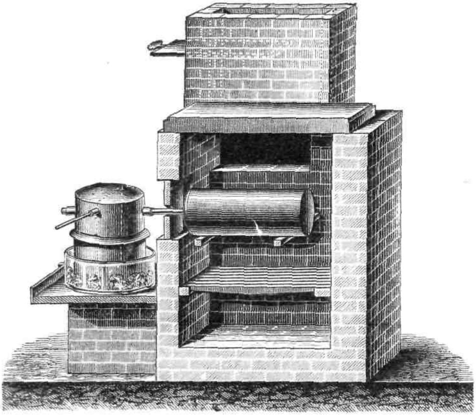


Fig. 59.

retort is afterwards heated to whiteness in a furnace, and the potassium vapour which distils over condensed in a suitable receiver.

One of the wrought-iron bottles in which mercury is imported answers well for the retort. It lies in the furnace in a horizontal position, supported on iron bars, as shown in fig. 59. A short wide iron tube, open at both ends, is screwed air-tight into the retort and leads to the upper part of the receiver, which contains a little naphtha, and is cooled externally by ice. The potassium then condenses in the receiver and collects under the naphtha.

The operation is not without danger, for the iron tube may easily

become plugged with substances less volatile than the potassium, and so produce a violent explosion. Great care must therefore be taken to keep this tube free from obstruction. This can be done by frequently inserting an iron wire bent into a corkscrew shape through a hole in the condenser into the tube and moving it backwards and forwards.[1]

The potassium which condenses in the receiver is afterwards rectified by distilling it in an earthenware retort, or in one of hard glass, covered externally with a layer of clay. It is thus obtained in small pellets of about the size of a hazel-nut, which, if kept under naphtha in well-closed bottles, can be preserved for a long time. They are generally coated with a thin brownish crust.

If potassium is exposed to the air it takes up oxygen, water, and carbonic acid, with evolution of heat, and becomes converted into a mixture of potassium hydrate (caustic potash) and potassium carbonate, which gradually becomes a syrupy solution of potassium carbonate :—

$$2K + 2H_2O = 2KOH + H_2$$

and

$$2KOH + CO_2 = CO(OK)_2 + H_2O.$$

When heated in the air potassium burns with a violet flame and produces its peroxide. The metal decomposes water at the ordinary temperature with a large evolution of heat, and appears to burn with a violet flame when thrown upon water. What really burns is the hydrogen which the potassium liberates from the water in its conversion into potassium hydrate, and which is ignited by the large amount of heat evolved during the reaction. The violet colour of the burning hydrogen is due to small particles of potassium with which it is mixed.

Potassium also burns in chlorine, and forms potassium chloride. At the ordinary temperature it does not unite with hydrogen. But at 200°, and especially between 300° and 400°, it begins to absorb the gas and becomes changed into a lustrous, brittle, crystalline substance, which catches fire on exposure to the air, and is again decomposed at a higher temperature. This compound may have the composition : K_2H.

[1] Violent explosions are also sometimes produced in the manufacture of potassium by the formation of a peculiar black compound of potassium and carbon which very easily decomposes. These explosions may be prevented if the potassium vapour is rapidly cooled by attaching a flattened receiver to the iron delivery tube. This exposes a large surface to the air and so rapidly cools the hot vapour.—ED.

COMPOUNDS OF POTASSIUM.

Potassium unites with oxygen in at least two proportions, to form *potassium monoxide*: K_2O, and *potassium peroxide*: K_2O_4. Oxides having the respective formulæ: K_2O_2 and K_2O_3 have also been said to have been prepared. All these compounds are only of theoretical interest.

If potassium is heated in dry oxygen or air, it forms not the oxide but a yellow powder, which consists of the higher oxides of potassium. These oxides are decomposed by water, or even by exposure to moist air, forming caustic potash, and giving off oxygen.

Potassium monoxide: K_2O, can be obtained by treating thin layers of potassium in the cold with oxygen, but is best prepared by fusing caustic potash with as much potassium as it already contains: $KOH + K = K_2O + H$. It is a white powder, which melts at a red-heat, energetically attracts moisture from the air, and in contact with water becomes converted into potassium hydrate, with a large evolution of heat: $K_2O + H_2O = 2KOH$.

Potassium Hydrate, Caustic Potash: KOH.—This important compound is a white crystalline solid, melting to a clear liquid at a red-heat. It is strongly alkaline and caustic, deliquesces in the air, and is easily soluble both in water and alcohol.

An aqueous solution of pure potassium hydrate may be obtained by dropping small pieces of potassium into water. And from this solution the solid may be prepared by rapidly evaporating the liquid in a silver basin, silver being much less attacked by caustic potash than platinum.

The ordinary method for the preparation of caustic potash on the large scale consists in dissolving potassium carbonate in about eight or ten times as much water, heating the solution in an iron vessel to boiling, and then gradually adding slaked-lime which has been previously mixed with water to a thin paste. The lime then combines with the carbonic acid, forming calcium carbonate, which is insoluble in water, and caustic potash remains in solution. A more concentrated solution of potassium carbonate cannot be employed, because it would only be incompletely de-

composed by the lime. Strong caustic potash decomposes calcium carbonate when boiled with it, forming potassium carbonate and lime. The quantity of quick-lime (calcium oxide) which is required to convert a given weight of potassium carbonate into potassium hydrate is calculated according to the following equation :—

$$CO(OK)_2 \quad + \quad CaO \quad + \quad H_2O \quad = \quad CO{\cdot}O_2Ca \quad + \quad 2KOH,$$

and weighed out. This lime is next slaked, mixed with water, and the milk of lime dropped into the boiling potassium carbonate until a small quantity of the clear liquid no longer effervesces with hydrochloric acid—a proof that it no longer contains potassium carbonate. The fire is then removed, the vessel covered with an iron lid and allowed to cool. As soon as the calcium carbonate has settled, and the liquid become clear, it is run off with a syphon, and rapidly evaporated in a clean iron or silver dish, when solid crystalline potassium hydrate remains behind.

Potassium hydrate appears to form several crystalline compounds with water, and the solid commercial hydrate usually contains more or less water, up to 20 per cent. This water may be removed by heating the compound in a silver dish until it fuses quietly. A saturated aqueous solution of potassium hydrate deposits crystals on cooling, consisting of one molecule of the hydrate united with two of water : $KOH + 2H_2O$.

Caustic potash prepared in this way is never pure. It contains firstly the impurities present in the commercial potassium carbonate, such as potassium chloride, sulphate, &c. ; secondly, the impurities of the crude lime ; and, thirdly, potassium carbonate, due to the absorption of carbonic acid from the air during the evaporation of the solution. To prepare the pure substance from the crude hydrate, it is broken into pieces and shaken up in a closed vessel with cold alcohol. This liquid dissolves the potassium hydrate, but leaves all the impurities, including the potassium carbonate, behind undissolved. The clear solution is then run off, diluted with water, and heated, first to drive off the alcohol and then more strongly to expel the water. If the alcoholic solution were heated alone without the addition of water, the liquid would be decomposed under the influence of the potash and the oxygen of the air, and would acquire a brown colour and unpleasant odour.

Small quantities of chemically pure potassium hydrate may be

prepared by boiling a solution of pure potassium carbonate with pure lime obtained from Iceland spar or white marble. But as caustic potash, as well as its solution, readily dissolves both silica and alumina, it can neither be prepared nor evaporated in vessels of glass or porcelain; it energetically attacks both these substances.

The fused caustic potash of commerce is the hydrate which has been melted and strongly heated as long as it loses water. It is sometimes brought into trade in the form of rough flat pieces, showing a crystalline fracture, or else as sticks of about the thickness of a black-lead pencil, which are obtained by casting the fused substance in iron moulds made in two pieces (see fig. 60).

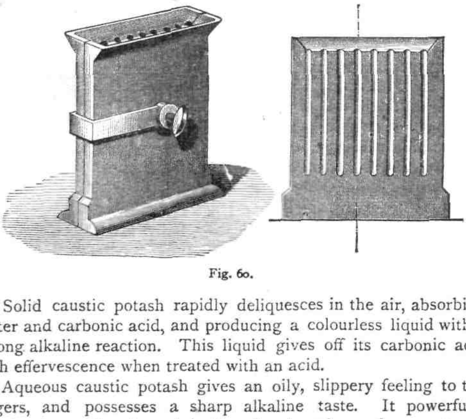


Fig. 60.

Solid caustic potash rapidly deliquesces in the air, absorbing water and carbonic acid, and producing a colourless liquid with a strong alkaline reaction. This liquid gives off its carbonic acid with effervescence when treated with an acid.

Aqueous caustic potash gives an oily, slippery feeling to the fingers, and possesses a sharp alkaline taste. It powerfully attacks the epidermis, and is therefore largely used as a strong caustic. The solution dissolves grease and fats, with which the alkali unites and forms soluble compounds called *soaps*; a dilute potash lye (or solution of the alkali) is therefore employed for cleansing purposes.

Caustic potash, both in the solid form and in solution, is largely used in the laboratory. In its attraction for acids it

excels all other bases,[1] and is, therefore, the most suitable substance to separate them from their salts. If a solution of a salt of copper, for example, is mixed with caustic potash, the corresponding potassium salt is produced, and copper hydrate separates as a precipitate :—

$$SO_2 \cdot O_2Cu \quad + \quad 2KOH \quad = \quad SO_2(OK)_2 \quad + \quad Cu(OH)_2.$$

Caustic potash is also largely used in the arts, but is gradually becoming displaced by the cheaper caustic soda, except when the latter is too feeble to effect the required change—for example, in the conversion of cellulose into oxalic acid (see p. 298).[2]

The *salts of potassium* can be easily prepared by the union of the base with the corresponding acid. In this small text-book we can only refer to the most important of this numerous class of compounds.

Potassium Sulphate : $SO_2\begin{cases}OK\\OK\end{cases}$ is easily obtained by neutralizing potassium carbonate with sulphuric acid, and crystallizes when a concentrated solution is allowed to cool in hard four-sided pyramids or prisms, without water of crystallization. It possesses a saline, bitter taste, and melts when strongly heated without change. It is not so easily soluble in water as the other potassium salts : 100 parts of water at 12° only dissolve twelve parts of the salt, and at 100° only twenty-six parts. Alcohol does not dissolve it in the least.

Acid Potassium Sulphate : $SO_2\begin{cases}OH\\OK\end{cases}$ is prepared by heating the normal sulphate with the requisite quantity of sulphuric acid, and is a bye-product when nitric acid is manufactured from potassium nitrate (p. 190). It is easily soluble in water, and crystallizes from the hot concentrated solution in rhombohedra ; it reacts and tastes acid. When heated to about 200°, it melts quietly ; at a higher temperature it gives off water, and is converted into potassium disulphate like the sodium salt (p. 167) :—

$$2SO_2\begin{cases}OH\\OK\end{cases} \quad = \quad O\begin{cases}SO_2OK\\SO_2OK\end{cases} \quad + \quad H_2O.$$

[1] Except the oxides of the rare metals rubidium and cæsium.—ED.

[2] Owing to the large quantities of caustic potash now sent into trade from the German manufactories, its present retail price is the same as that of caustic soda.—ED.

At a still higher temperature this salt splits up into sulphuric anhydride and the normal sulphate. Hence the use of acid potassium sulphate to decompose certain minerals which are not attacked by acids.

Potassium Nitrate (*Nitre*, *Saltpetre*): $NO_2 \cdot OK$, crystallizes from a hot solution in long, furrowed, rhombic prisms, with a saline cool taste, and may be easily prepared by neutralizing nitric acid with potassium carbonate and evaporating down. Nitre is also produced naturally in countries where the soil is rich in potassium salts and where rain seldom falls, or only at periodic intervals (Egypt, Persia, India, &c.). In these countries the surface of the ground after the rains gradually becomes covered with a white efflorescence, which consists chiefly of potassium nitrate. The salt is then obtained by simple solution in water and re-crystallization. This nitre owes its production to the potassium salts and nitrogenous organic matter present in the soil. The latter gradually undergoes decay, and its nitrogen is converted into ammonia, which, in the presence of the strong base, becomes oxidized to nitric acid, forming potassium nitrate.

This process has been imitated in some European countries, and large quantities of nitre have been artificially produced in the following manner. Heaps of earth mixed with some potassium carbonate and lime were made under open sheds and then repeatedly watered with liquid manure or other nitrogenous organic refuse. The mass was frequently turned so as to expose it as much as possible to the oxidizing influence of the air. After a considerable period (often one or more years), when all the nitrogen had been converted into nitrates, the heaps were lixiviated with water to dissolve these soluble salts, and the solution mixed with potassium carbonate to convert the calcium and magnesium nitrates into the soluble potassium salt. The clear solution was then run off from the insoluble calcium and magnesium carbonates and evaporated down to crystallize.[1]

Considerable quantities of potassium nitrate are now prepared from the sodium nitrate found so largely in Chili. If a solution

[1] This production of nitre from nitrogenous organic substances is exceedingly costly and wasteful, since the value of the nitrogen in the form of ammonia for increasing the fertility of the soil is far greater than that of the nitre obtained from it, and the process has now been almost entirely abandoned.—ED.

of this salt is mixed with one of potassium chloride, and the mixed solution evaporated down under pressure, double decomposition occurs into sodium chloride (common salt) and potassium nitrate. And since sodium chloride is only slightly more soluble in hot than in cold water, this salt first separates out on evaporating, while potassium nitrate, which is much more soluble in hot than in cold water, crystallizes out on cooling the hot decanted liquid.

Potassium nitrate prepared in any of these ways is always mixed with impurities, especially common salt, from which it can be freed by repeated crystallization. This purification depends upon the greater solubility of saltpetre in hot than in cold water. 100 parts of water dissolve only 13 parts of the salt at 0°, and 29 parts at 18°, but at 97° the same quantity of water dissolves 236 parts. And a boiling-hot saturated solution of saltpetre, of which the boiling-point is 116°, is said to contain 335 parts of the salt dissolved in 100 parts of water.

Nitre is used for various purposes in medicine, and sometimes for the manufacture of nitric acid, but far larger quantities are absorbed in the manufacture of gunpowder, in which the nitre is the oxidizing substance. The well-known explosive action of gunpowder is due to the sudden production of large volumes of hot gases from a small volume of a solid. If powdered nitre is sprinkled on a piece of glowing charcoal, the latter burns brilliantly to carbonic acid and carbonic oxide, while the nitre is converted into potassium carbonate and free nitrogen. The same process goes on when an intimate mixture of powdered nitre and charcoal, in the correct proportions, is ignited, and may be represented by the following equation :—

$$2NO_2\cdot OK + 3C = CO_2 + CO + N_2 + CO\begin{cases}OK\\OK\end{cases}$$

Gunpowder contains, however, sulphur as well as nitre and charcoal, and it was formerly thought that its decomposition when burnt was expressed by the equation :—

$$2NO_2\cdot OK + 3C + S = 3CO_2 + N_2 + K_2S,$$

which represents the various constituents in the proportions in which they are actually contained in gunpowder. But it has been found that other substances, besides those shown in the above equation, are also produced, and that the sulphide formed is potassium disulphide and not the monosulphide. The substances into which gunpowder is converted when burnt in a closed space are essentially :—

(i.) *Solids*, including potassium carbonate, potassium sulphate, and potassium disulphide, and which are about 57 per cent. of the whole.

(ii.) *Gases* which consist of carbonic acid, nitrogen, and carbonic oxide, and constitute the remaining 43 per cent. by weight. The volume of these gases, measured at the normal temperature and pressure, is nearly 300 times that of the powder, and at the high temperature of the explosion nearly 2,000 times. Hence the force of the explosion. Other substances are also formed when gunpowder is exploded, but only in very small quantities. And the actual chemical changes which go on when the powder is burnt can only be represented by a somewhat complex equation.

The gunpowder of different countries, and even of the same country, varies considerably. The mean composition of English powder is about as follows :—

Nitre	75·3
Charcoal	13·4
Sulphur	11·3
	100·0

In the manufacture of a suitable gunpowder it is not only necessary to mix the constituents intimately together, but the mixture must be afterwards granulated, an operation which is performed by suitable machinery. The size of the grain depends upon the purpose for which the powder is to be used : it varies from about the size of a millet seed for ordinary purposes and small arms, up to blocks as large as a cubic inch (pebble powder) for large cannon.

By diminishing the quantity of nitre, and increasing that of charcoal or sulphur, the rate at which the powder burns is diminished. And as the gases produced by the burning of the powder cannot support combustion, but, on the contrary, extinguish bodies in the act of burning, this property has been successfully utilized to extinguish fires in closed places. A mixture for this purpose may contain, for example, 60 to 66 per cent. nitre, 30 to 36 per cent. sulphur, and at most 4 per cent. charcoal. On burning, it produces sulphurous anhydride with carbonic acid and nitrogen, all of which extinguish burning bodies.

Potassium Nitrite: NO·OK.—If potassium nitrate is melted at a low red heat, it is decomposed into oxygen which escapes, and potassium nitrite which remains behind, usually mixed either with

undecomposed nitrate, or, if too strongly heated, with caustic potash. The salt is easily soluble in water, deliquesces in the air, and evolves copious red vapours of nitrous acid when treated with moderately dilute sulphuric acid.

Potassium Carbonate : $CO\begin{cases}OK\\OK\end{cases}$ deliquesces in the air and is easily soluble in water. The aqueous solution reacts strongly alkaline, and when evaporated down leaves the salt as a white solid which melts unchanged at high temperatures. An extremely concentrated, warm solution deposits crystals containing about 16 per cent. of water of the composition: $2CO\begin{cases}OK\\OK\end{cases} + 3H_2O$.

Potassium carbonate is a constituent of the ashes which remain when wood and land plants generally are burnt, which, however, do not contain more than 20 per cent. of it. The ashes consist chiefly of the sulphates, phosphates, and silicates of potash, lime, and magnesia, together with some chlorides.

Crude potash is obtained by extracting the ashes with water, and evaporating the filtered solution to dryness. It contains at most 60 per cent. of potassium carbonate mixed with the other soluble salts contained in the ashes. By digesting this crude potash with an equal weight of water for several days, with frequent stirring, the easily soluble carbonate is dissolved, leaving most of the other salts behind. The clear solution evaporated to dryness gives the *pearlash* of commerce.

This is still very far from pure potassium carbonate, and in fact we know of no method of completely purifying it. Chemically pure potassium carbonate may, however, be easily obtained by heating a pure potassium salt of an organic acid in a platinum vessel. Vessels of porcelain or glass cannot be employed, as the hot potassium carbonate abstracts silica from them, and so becomes impure. For the preparation of the pure salt, acid potassium tartrate is commonly used. This salt can be readily obtained, and, as it is only difficultly soluble in water, can be easily purified. The heated mass, when extracted with water, and the clear solution evaporated in a platinum dish, leaves pure potassium carbonate as a snow-white solid.

Since the discovery of the potassium chloride beds at Stassfurth, potassium carbonate is manufactured from the chloride, just as soda is obtained from common salt by Leblanc's process (see p. 371).

Potassium carbonate is one of the most important of the potassium salts. It is used not only for the preparation of caustic potash and many other potassium compounds, but is also largely employed in the arts, especially in the manufacture of glass and of soft soap.

Acid Potassium Carbonate: $CO\begin{cases}OH\\OK\end{cases}$ is obtained by leading carbonic acid into a concentrated aqueous solution of the normal salt, when it separates out as a crystalline powder :—

$$CO\begin{cases}OK\\OK\end{cases} + CO_2 + H_2O = 2CO\begin{cases}OK\\OH\end{cases}$$

It requires about four times its weight of water for solution, reacts neutral, and is decomposed at about 80° into the normal salt and carbonic acid.

Potassium Chlorate: $ClO_2 \cdot OK$.—This salt, of which the preparation has been already described (p. 110), crystallizes when its hot saturated solution is cooled in lustrous scales or larger plates. It melts at 334°, and begins to be decomposed, with evolution of oxygen, at 352°. It requires 16 parts of water for solution at the ordinary temperature, but only 2 parts at 100°. In consequence of the readiness with which it parts with oxygen, it is an excellent oxidizing agent, and yields considerable quantities of chlorine when warmed with hydrochloric acid (p. 112).

Potassium Perchlorate: $ClO_3 \cdot OK$, has been already described. It belongs to the potassium salts which are difficultly soluble in water, and can, therefore, be readily purified by crystallization. The salt is insoluble in alcohol.

Potassium Hypochlorite: ClOK.—This salt, which is only known in its aqueous solution and which is characterized by its powerful bleaching properties, is obtained by passing chlorine into a cold, dilute solution of potassium carbonate until large quantities of carbonic acid are evolved. Potassium chloride and hypochlorite with acid potassium carbonate are first produced :—

$$2CO\begin{cases}OK\\OK\end{cases} + 2Cl + H_2O = 2CO\begin{cases}OK\\OH\end{cases} + KCl + ClOK,$$

and carbonic acid is, therefore, not evolved at once, but only when the chlorine begins to attack the acid potassium carbonate.

This solution of potassium hypochlorite is known as *eau de Javelle.* Strong acids liberate considerable quantities of chlorine from it.

Potassium Oxalate : $\left\{\begin{matrix} CO\cdot OK \\ CO\cdot OK \end{matrix}\right. + H_2O$. The normal salt is obtained by neutralizing oxalic acid, or the acid salt, with potassium carbonate, and easily crystallizes from its aqueous solution. The *acid salt*: $\left\{\begin{matrix} CO\cdot OH \\ CO\cdot OK \end{matrix}\right. + H_2O$ (*salts of sorrel*), occurs in some plants, especially in the leaves of the sorrels, from which it may be obtained in large crystals by pressing the leaves and evaporating the acid juice. It has a strong acid reaction, and unites with ferric oxide to form a soluble double salt. Hence its use to remove ink or iron stains from paper or linen. After the stains have been removed, the fabric must be carefully washed, first with water and then with dilute soda, to prevent corrosion by the oxalic acid contained in the acid salt. Besides this acid salt, a so-called diacid salt (potassium quadroxalate) is also known. The salt crystallizes well, and is to be considered as a double compound of acid potassium oxalate and oxalic acid :—

$$\left\{\begin{matrix} CO\cdot OK \\ CO\cdot OH \end{matrix}\right. + \left\{\begin{matrix} CO\cdot OH \\ CO\cdot OH \end{matrix}\right. + 2H_2O.$$

Potassium Silicate (potash water-glass).—Silica and caustic potash or potassium carbonate may be fused together in varying proportions, and produce, when the quantity of silica is not too great, a glass which is distinguished from ordinary glass by its solubility in water. Hence the name *water-glass.* It may be obtained by melting together equal weights of pearlash and sand until the mass fuses quietly, or by dissolving infusorial earth in caustic potash. By the latter operation a solution is at once obtained. In England considerable quantities of water glass are manufactured by heating powdered flints with caustic potash (or soda) under pressure, when the flints readily dissolve. On evaporating a solution of water-glass, an amorphous transparent mass remains behind, which, when exposed to the air, gradually becomes covered with an opaque coating of silicic acid and potassium carbonate. The solid fused water-glass undergoes the same decomposition.

An aqueous solution of water-glass has many technical applications. It is used, for example, to render theatrical scenes and

other stage appliances uninflammable. Such articles when coated with a thin layer of water-glass are no longer combustible; the thin layer of potassium silicate protects their surface like a varnish from the oxygen of the air. If brought into contact with a burning body they become charred but do not catch fire. Water-glass is also largely used for protecting buildings from damp, for preventing the decay of woodwork in damp situations, and very largely in the manufacture of the cheaper kinds of soap.

In a very dilute aqueous solution potassium silicate forms a valuable manure for many plants, especially for those which require potash salts and silica for their growth. Pasture lands are improved by occasionally watering with a dilute solution of potash water-glass.

It has already been mentioned that potassium silicate is a constituent of many minerals—for example, of felspar.

Potassium Chloride: KCl, crystallizes like sodium chloride in the regular system, and usually in cubes without water of crystallization. The crystals contain, however, water mixed mechanically, which causes them to decrepitate when heated. It has a saline taste, and is tolerably soluble in water: 100 parts of water dissolve about 33 parts of the salt at the ordinary temperature, and hot water only a little more. It melts without change when heated to redness, and then volatilizes in not inconsiderable quantities. Potassium chloride is a constituent of sea-water, is contained in the ashes of land plants, and is also found in large quantities as a mineral. It is the chief constituent of the salt beds in the neighbourhood of Stassfurth in Northern Germany. The mineral *sylvin* consists almost exclusively of it.

Potassium Bromide: KBr, closely resembling potassium chloride, may be prepared by neutralizing potassium carbonate with hydrobromic acid, or by saturating caustic potash with bromine, evaporating to dryness, and then glowing to destroy the potassium bromate produced at the same time. It is now largely used in medicine for neuralgic affections.

Potassium Iodide: KI.—This salt resembles potassium chloride in its external properties. Like the chloride, it crystallizes in cubes without water. It is, however, much more easily soluble in

water than potassium chloride, and thus remains in the mother-liquor when a mixed solution of the two salts is evaporated down. At the ordinary temperature 100 parts of water dissolve more than 140 parts of potassium iodide; the saturated solution contains, at its boiling-point (120°), more than 200 parts of potassium iodide for every 100 parts of water.

Potassium iodide is of such importance in medicine and photography that many attempts have been made to discover profitable and ready methods for preparing it. The simplest method—viz neutralization of caustic potash or potassium carbonate with hydriodic acid, just as potassium chloride may be obtained—is impracticable, because hydriodic acid is very much more difficult to obtain in quantity than hydrochloric acid.

Two methods are chiefly used for the preparation of potassium iodide. One consists in gradually adding iodine to warm caustic potash until the liquid becomes yellow from free iodine, evaporating the liquid, which now contains potassium iodide and iodate (p. 130), to dryness, and glowing, in order to convert the potassium iodate into potassium iodide and oxygen. It has been found, however, that a much higher temperature is required to decompose potassium iodate than potassium chlorate, and at this high temperature some of the potassium iodide is volatilized and lost. It is therefore customary to add a little powdered wood charcoal to the liquid containing the mixed salts. When the saline mass is afterwards glowed, this charcoal abstracts all the oxygen from the iodate and is converted into carbonic acid. The residue is then extracted with water, and the clear solution evaporated down to crystallize.

A second method largely used for the preparation of potassium iodide is as follows. One part of iron filings is mixed with water and digested with three parts of iodine, when the two substances readily unite with one another, with considerable rise in temperature, and produce the easily soluble salt—ferrous iodide: FeI_2. As soon as all the iodine has disappeared, the green solution is filtered, and one more part of iodine added, which produces the compound ferroso-ferric iodide, FeI_2, Fe_2I_6. The liquid is then exactly precipitated with potassium carbonate, when ferroso-ferric hydrate easily separates and can be readily washed, and the clear solution, which now contains potassium iodide, is evaporated down to crystallize. From 4 parts of iodine, 5 parts of potassium iodide may be thus obtained. The ferrous iodide might be at once decomposed by potassium carbonate, but the precipitate then

consists of ferrous carbonate, which does not readily settle, and *can only be washed with difficulty, and therefore requires large* quantities of water and a long time to extract all the potassium iodide.

An aqueous solution of potassium iodide dissolves large quantities of free iodine; the saturated solution contains about twice as much iodine as was present in the original salt, producing the compound: KI_3, which may be obtained as dark, lustrous needles, on careful evaporation. This compound is very deliquescent, and easily decomposes into potassium iodide and iodine.

Potassium iodide, together with the sodium salt, is present in many mineral waters, and especially in the ashes of sea plants (pp. 123, *et seq.*). It is largely used in medicine as a remedy for goître and swellings, in cases of syphilis, &c., and is, in fact, one of the most highly prized medicines. Large quantities of the salt are also used in photography.

Potassium Fluoride: KF, is easily obtained by neutralizing hydrofluoric acid with potassium carbonate. It crystallizes at the ordinary temperature with two molecules of water, but above 35° without water, in cubes; the salt easily deliquesces in moist air, and strongly attacks glass.

Potassium fluoride unites with other fluorides and with hydrofluoric acid, and produces double salts, in which the fluorine appears to play the part of a diad.

Acid Potassium Fluoride: HKF_2.—This salt is easily prepared by neutralizing a given volume of aqueous hydrofluoric acid with potassium carbonate, and then adding an equal volume of the acid. It crystallizes out when the solution is evaporated down in a platinum basin. The crystals are anhydrous; they easily dissolve in water, but difficultly in that containing hydrofluoric acid. It requires heating to redness before it is decomposed into potassium fluoride and hydrofluoric acid.

Potassium Fluoborate: $KF,BF_3 = KBF_4$, is precipitated as a gelatinous, iridescent mass, which dries to a white impalpable powder when potassium fluoride, or any other soluble potassium salt, is mixed with aqueous fluoboric acid. It is difficultly soluble in cold water, of which it requires 70 times its weight for solution.

Potassium Fluosilicate: $2KF,SiF_4 = K_2SiF_6$, closely resembles the fluorborate, but is still less soluble in water. Potassium fluosilicate is therefore sometimes used as a test for potassium.

Potassium Cyanide: $KCN = KCy$.—This extremely poisonous salt is decomposed by all acids, including carbonic acid, giving free hydrocyanic acid. It may be obtained pure by passing hydrocyanic acid gas into well-cooled alcoholic potash, until the mass becomes pasty from separation of the potassium cyanide, which is almost insoluble in alcohol. The crystalline mass is then brought on a filter, quickly washed with strong alcohol, as much of the liquid removed as possible by a filter-pump, and finally dried in a vacuum over sulphuric acid.

The less pure compact potassium cyanide of commerce, which occurs as flat pieces with a crystalline fracture, is prepared by a much less expensive process. Potassium ferrocyanide: $K_4FeCy_6 + 3H_2O$, which may be considered as a double cyanide of ferrous iron and potassium: $4KCy, FeCy_2 + 3H_2O$, is first thoroughly freed of its water of crystallization by powdering it and heating it in a shallow iron dish. The dried salt is then placed in an iron crucible, which it must not more than two-thirds fill, and heated to fusion in a furnace. The ferrous cyanide is then decomposed into nitrogen gas which is given off, and black iron carbide which remains behind. The potassium cyanide melts unchanged, provided it is not exposed to the air, from which (when in the fused state) it readily absorbs oxygen, and becomes partly converted into potassium cyanate. As soon as the salt fuses quietly, the crucible is removed from the furnace, and repeatedly knocked on some hard body that the iron carbide may settle to the bottom and the potassium cyanide become clear. When the fused salt has sufficiently clarified, which may be easily known by removing a drop on the end of a glass rod, the liquid is carefully poured on to an iron slab, broken into pieces when cold, and preserved in well-closed vessels.

In this method of preparation two of the six atoms of cyanogen contained in a molecule of potassium ferrocyanide are lost: the two atoms combined with the iron are decomposed. In order to obtain this cyanogen as well, it is best to use Liebig's method, which consists in mixing every 8 parts of the dry potassium ferrocyanide with 3 parts of potassium carbonate. When this mixture is melted, the ferrous cyanide of the potassium ferrocyanide and

the potassium carbonate first form ferrous carbonate and potassium cyanide :—

$$FeCy_2 \quad + \quad CO\begin{cases}OK\\OK\end{cases} \quad = \quad 2KCy \quad + \quad CO\cdot O_2Fe.$$

But the ferrous carbonate is at once broken up at the high temperature into carbonic acid and ferrous oxide :—

$$CO\cdot O_2Fe \quad = \quad CO_2 \quad + \quad FeO,$$

the oxide being finally reduced to metallic iron by a portion of the potassium cyanide, which is converted into potassium cyanate. Thus, of the two atoms of cyanogen which were united with the iron, one is obtained as potassium cyanide and one as potassium cyanate.

As this small quantity of potassium cyanate is without importance for most of the technical purposes for which potassium cyanide is used, the commercial salt is now always manufactured by Liebig's process. The quantity obtained is not only larger, but the product is also whiter.

Potassium cyanide is very easily soluble in water, and deliquesces in moist air. From its aqueous solution it can, by evaporation over sulphuric acid, be crystallized in cubes; but, if the solution be heated, it gradually decomposes into potassium formate and ammonia :—

$$KCN \quad + \quad 2H_2O \quad = \quad \begin{cases}H\\CO\cdot OK\end{cases} \quad + \quad NH_3.$$

It is scarcely soluble in alcohol. The aqueous solution reacts alkaline, and plays the part of a base with many other insoluble cyanides. Just in the same way as potassium hydrate dissolves lead oxide, alumina, and silica, producing salts in which these substances take the part of an acid, so, too, potassium cyanide dissolves lead cyanide, silver cyanide, and numerous other similar insoluble compounds, forming salts which are soluble in water, and can usually be obtained in the crystalline state.

Neither solid potassium cyanide nor its aqueous solution unites directly with oxygen. But in the fused state its attraction for oxygen is so great that most of the metallic oxides are decomposed by it. The substance produced by this oxidation is potassium cyanate. The salt also easily combines directly with sulphur, forming potassium sulphocyanate. Union of the two substances even takes place when flowers of sulphur are stirred up with a warm aqueous solution of potassium cyanide.

Potassium Cyanate : KOCN.—This white crystalline salt is easily soluble both in water and alcohol, and may be purified by crystallizing from the latter liquid. It is obtained by adding an oxide of lead to fused potassium cyanide, when the oxide is reduced to metallic lead and the cyanide oxidized to cyanate. It is, however, best prepared directly from potassium ferrocyanide by oxidization with manganese peroxide.

Well dried and finely powdered potassium ferrocyanide is thoroughly mixed with an equal weight of dry commercial manganese peroxide containing about 75 per cent. of the pure compound, and the mixture gently heated with continual stirring in a flat iron dish. After a little time the mass begins to glow ; the heating is continued as long as this lasts and until a fragment when dissolved in water gives no precipitate of Prussian blue on mixing the clear solution with ferric chloride.

The mass is next repeatedly digested with strong alcohol (82 per cent.), and potassium cyanate then separates from the hot saturated solution on cooling as thin tablets. After filtering off the crystals, they must be rapidly dried, as potassium cyanate readily decomposes with water, even at the ordinary temperature, into potassium and ammonium carbonates :—

$$2KOCN + 4H_2O = CO(OK)_2 + CO(ONH_4)_2.$$

Its aqueous solution, when mixed with ammonium sulphate, forms potassium sulphate and ammonium cyanate, which latter changes immediately into the isomeric compound urea. Addition of a strong acid to a solution of potassium cyanate does not liberate free cyanic acid, but decomposes it into carbonic acid and ammonia (p. 317).

Potassium Sulphocyanate: KSCN, may be obtained by adding sulphur to fused potassium cyanide, or, better, by heating a mixture of 46 parts of potassium ferrocyanide, 17 parts of potassium carbonate, and 32 parts of sulphur in a Hessian crucible until the mass fuses quietly, and until a drop dissolved in water no longer gives a blue precipitate with ferric chloride, but only a red colour. The fused mass is broken in pieces when cold and digested with hot alcohol, which dissolves the potassium sulphocyanate and leaves ferrous sulphide behind. From the hot solution it crystallizes on cooling in long colourless crystals, resembling nitre, and possessing, like this salt, a cooling taste.

Water dissolves large quantities of it, so that it deliquesces in moist air. A considerable fall in temperature is produced when the salt is dissolved in water.

Potassium sulphocyanate, or any soluble sulphocyanate, gives no precipitate with ferric salts, but a deep red colour.

Compounds of Potassium with Sulphur.

The alkali metals unite with sulphur in several proportions, forming definite chemical compounds, which may be compared with the compound of potassium iodide with iodine. Just as potassium iodide unites with two atoms of iodine (p. 359), so also potassium sulphide unites with one, two, three, and four atoms of sulphur, producing the compounds :—

Potassium disulphide	K_2S_2
Potassium trisulphide	K_2S_3
Potassium tetrasulphide	K_2S_4
Potassium pentasulphide	K_2S_5.

The two atoms of potassium do not appear to combine with more than five atoms of sulphur.

Potassium Monosulphide: K_2S, is a strong sulpho-base, easily soluble in water, and deliquescing in the air. It has a strong alkaline reaction and taste. This compound may be obtained by reducing potassium sulphate in a stream of hydrogen at a red-heat :—

$$SO_2(OK)_2 \ + \ 4H_2 \ = \ K_2S \ + \ 4H_2O,$$

or, better, by glowing a mixture of one molecule of the salt with four molecules of carbon :—

$$SO_2(OK)_2 \ + \ 4C \ = \ K_2S \ + \ 4CO.$$

A mixture of 3 parts of powdered potassium sulphate and 1 part of wood charcoal is placed in a covered Hessian crucible, which it must not more than two-thirds fill, and heated until the mixture has ceased frothing and fuses quietly. When the crucible is cold it is broken, and the potassium sulphide obtained as a red crystalline mass. It soon loses its colour in the air, from which it abstracts not only water, but also oxygen and carbonic acid.

An aqueous solution of potassium monosulphide is readily obtained in the following way. A given volume of moderately concentrated caustic potash is divided into two equal parts. One of

these is then completely saturated with sulphuretted hydrogen gas, which forms the sulphydrate: KSH, and the other part is then added. One molecule of potassium sulphydrate is decomposed by one molecule of caustic potash into one molecule of potassium monosulphide and one of water :—

$$KSH + KOH = K_2S + H_2O.$$

This solution is decomposed when treated with dilute acids, and then evolves sulphuretted hydrogen without depositing sulphur. It absorbs oxygen from the air, and is converted into potassium thiosulphate :—

$$K_2S + 3O = SO_2\begin{cases}OK\\SK\end{cases}$$

Potassium monosulphide easily dissolves the sulphides of arsenic, antimony, and carbon and other similar sulpho-acids, with which it unites chemically and forms soluble sulpho-salts.

Potassium Sulphydrate: KSH or $\left.\begin{matrix}K\\H\end{matrix}\right\}S$. This compound, which corresponds to caustic potash, is obtained by leading sulphuretted hydrogen into caustic potash as long as the gas is absorbed. If the solution of caustic potash is sufficiently concentrated, the compound separates out on cooling in long colourless crystals, containing water of crystallization. In its chemical behaviour it closely resembles the monosulphide.

The *polysulphides of potassium* are obtained by adding the requisite quantity of sulphur to the fused monosulphide, or to its concentrated aqueous solution. If more sulphur is added to fused potassium monosulphide than corresponds to 4 molecules of the former to 1 molecule of the latter, there is produced

Potassium Pentasulphide: K_2S_5, and the excess of sulphur volatilizes. This compound has a yellow-brown colour ; it easily dissolves in water, and when acted on by hydrochloric acid yields sulphuretted hydrogen and large quantities of milk of sulphur (p. 145). When heated more strongly it loses sulphur and becomes

Potassium Trisulphide: K_2S_3, a compound closely resembling the pentasulphide.

Liver of Sulphur (*Potassa sulphurata.*)—This pharmaceutical preparation, which owes its name to its colour, consists essen-

tially of a mixture of potassium pentasulphide and potassium sulphate. It is prepared by gradually heating a mixture of about equal parts of potassium carbonate and sulphur in a large earthenware crucible. At first considerable quantities of carbonic acid are evolved, which causes the mixture to froth up ; as soon as this has ceased, the crucible is closed and the temperature gradually raised until all fuses quietly. The liquid is then poured on to a sheet of iron, broken into pieces when cold, and quickly brought into well-closed bottles, as it readily attracts moisture from the air. The following equation represents the reaction (see Appendix):—

$$4CO(OK)_2 \quad + \quad 16S \quad = \quad 3K_2S_5 \quad + \quad SO_2(OK)_2 \quad + \quad 4CO_2.$$

The preparation, when well made, should dissolve in water to a nearly clear solution, and when mixed with hydrochloric acid should give sulphuretted hydrogen and large quantities of free sulphur.

A solution containing potassium pentasulphide and thiosulphate may be obtained by gradually adding flowers of sulphur to boiling caustic potash as long as the sulphur is dissolved :—

$$6KOH \quad + \quad 12S \quad = \quad 2K_2S_5 \quad + \quad SO_2\begin{cases}OK\\SK\end{cases} \quad + \quad 3H_2O.$$

Detection of Potassium Compounds.

Potassium compounds when heated in the Bunsen burner impart a characteristic violet colour to the flame. In the presence of sodium, even in small quantities, the intense yellow light emitted by this substance obscures the feeble potassium flame, and it is therefore not seen by the naked eye. But if the flame is viewed through a piece of blue cobalt glass, the yellow sodium light is absorbed by the blue of the glass, while the violet potassium light passes through the glass unchanged. The most certain way of detecting traces of potassium is by its spectrum, which consists essentially of two lines in the red and one in the violet. (See Table of Spectra.)

If a solution of potassium chloride or of any other soluble potassium compound (except the iodide) is mixed with platinic chloride, a *yellow crystalline precipitate of a double chloride of* potassium and platinum : $2KCl, PtCl_4$, or *potassium chlorplatinate* : K_2PtCl_6, is produced, which is slightly soluble in water, but insoluble in alcohol. The heavy metals, as well as the metals of the earths and alkaline earths, if present, must have been pre-

viously removed from the solution, and ammonium compounds destroyed by glowing. Sodium salts do not give this precipitate, as the corresponding sodium salt is soluble both in water and alcohol. This double chloride of potassium and platinum is decomposed on glowing into metallic platinum, gaseous chlorine, and potassium chloride. The last-named compound can be extracted with water, and easily obtained in cubic crystals.

If a *concentrated* solution of a potassium salt is mixed with a concentrated solution of tartaric acid in excess, and the mixture well shaken or stirred with a glass rod, a white crystalline precipitate of acid potassium tartrate is produced, which is first deposited on those parts of the glass vessel which have been touched by the rod. Sodium salts do not produce this precipitate, as the corresponding acid sodium tartrate is easily soluble in water.

SODIUM.

Chemical Symbol: Na.—*Atomic Weight*: 23·1.

Sodium, which is closely allied to potassium, is also found in nature in the form of a double silicate of aluminium as soda felspar or *albite*. It further occurs as the mineral *cryolite*: $6NaF, Al_2F_6$, which is worked both for soda and for alumina. But by far its most important natural compound is the chloride—*common salt* or *rock-salt*.

The preparation of sodium is carried on in just the same way as that of potassium, except that some powdered chalk is usually added to the mixed sodium carbonate and charcoal, to prevent fusion at the high temperature necessary for reduction. Since the affinity of sodium for oxygen is less than that of potassium, its reduction, according to the method described on p. 344, is easier and the yield is greater. There is also less danger of the formation of explosive compounds, as in the preparation of potassium. This is one reason why sodium is so much cheaper than potassium.

It is chiefly owing to the researches of St. Claire Deville, supported by Napoleon III., who, in attempting to prepare cheap aluminium by means of sodium, so perfected the method for the extraction of this metal that its price has fallen from 5*s*. per oz. to 8*s*. per lb. during the last thirty-five years. The present low price

of sodium is also partly due to the large quantities which are now used for the manufacture of metallic magnesium.

Commercial sodium comes into trade in the form of bars. When freshly cut the surface is of a silver-white colour, but it very rapidly tarnishes in the air, becoming covered with a layer of its oxide. At the ordinary temperature it is soft like wax, and can be easily moulded or pressed into any shape. The metal is lighter than water, but somewhat heavier than potassium—its specific gravity being 0·978. Its melting-point, which is also higher than that of potassium, is 96°. It catches fire when heated in the air, and burns with an intensely yellow flame. Water is easily decomposed by it with evolution of hydrogen, and the sodium hydrate which is produced at the same time dissolves in the water and gives it an alkaline reaction. The liberated hydrogen does not, however, ignite like that set free by the action of potassium on water, because the quantity of heat set free when sodium decomposes water is less than when the same decomposition is effected by potassium—the affinity of the former metal for oxygen being less than that of the latter. The liberated heat would, however, raise the temperature of the hydrogen to its ignition point, if it were not continually cooled by the movement of the fragment of sodium on the surface of the cold water. If hot water, at about 80°, instead of cold water, is used for the experiment, the hydrogen catches fire at once and burns with a yellow flame. Or, if the surface of the water is covered with a piece of filter-paper the movement of the pellet of sodium is prevented, and it remains in contact with only a small quantity of water; this then becomes so strongly heated that the hydrogen catches fire.

Potassium and sodium unite together and form an alloy which is liquid at the temperature of the air, and closely resembles mercury. This is a striking example of the law that the melting-point of an alloy is lower than that of its constituents.

Sodium, like potassium, unites chemically with hydrogen when heated up to about 300° in the gas. This compound is again decomposed at about 420°. If dry ammonia is led over gently heated sodium the gas is decomposed with the formation of *sodium amide*: $Na \cdot NH_2$, while hydrogen is set free. When fused, this compound has a greenish-blue colour, but solidifies to a pink crystalline mass.

COMPOUNDS OF SODIUM.

With few exceptions, the compounds of sodium closely resemble those of potassium, and we shall, therefore, only describe those in detail which differ essentially from the corresponding potassium compounds.

Sodium, when heated in dry oxygen or air, produces *sodium peroxide*: Na_2O_2, similar in its properties to the potassium compound. *Sodium oxide*: Na_2O, is obtained, like potassium oxide, by heating sodium hydrate with sodium.

Sodium Hydrate (*Caustic Soda*): NaOH.—This compound is so similar to potassium hydrate that the two cannot be externally distinguished from one another. The general behaviour and the preparation of the two substances is also the same, except that caustic soda is a less powerful base than caustic potash. In preparing caustic soda from crystalline sodium carbonate, according to the method described on p. 346, it must be remembered that the sodium salt contains about 60 per cent. of water, and not more than five parts of water should, therefore, be used to dissolve one part of the salt.

Sodium Sulphate: $SO_2\left\{\begin{matrix}ONa\\ONa\end{matrix}\right. + 10H_2O$.—This salt, commonly known as *Glauber's salt*, is occasionally found in the solid state in nature, but usually in solution in various mineral springs. Many of these springs, especially those of Marienbad, Carlsbad, and others, are highly valued on account of the mild aperient action of the sodium sulphate which they contain. Sodium sulphate may be easily obtained by neutralizing sodium carbonate with sulphuric acid, or by heating this acid with common salt. This latter process is largely carried on in alkali (soda) works, where common salt is first converted into sodium sulphate prior to its change into sodium carbonate. (See Appendix.)

Sodium sulphate crystallizes with ten molecules (*i.e.* 56 per cent. of water) in large colourless prisms, which, when heated, melt in their water of crystallization, and finally lose all their water. It is easily soluble in water but insoluble in alcohol. At 0°, 100 parts of water dissolve 12 parts of the salt, at 18° 48 parts, at 25° 100

parts, and at 33° as much as 322 parts. But above 33° the solubility diminishes, because the compound with ten molecules of water cannot exist above this temperature. It is then converted into the anhydrous salt, which is less soluble in water, and separates from the solution above 33° in rhombohedra. If a glass flask is filled with a warm saturated solution of sodium sulphate and the neck closed with a loosely-fitting plug of cotton-wool, the solution remains clear and liquid after it has been allowed to cool quietly. And no change is produced if the plug is carefully removed and the end of a glass rod which has been heated in a gas flame and allowed to cool is dipped into the liquid. But the slightest touch with the other end of the rod, by which particles of dust are brought into contact with the liquid, at once causes the crystallization of the *supersaturated* solution, with a corresponding rise in temperature due to the liberation of latent heat.

Acid Sodium Sulphate: $SO_2\begin{cases}OH\\ONa\end{cases}$ is prepared in the same way as the potassium salt, and is deposited from its warm solution in large transparent crystals, without water. At the ordinary temperature it crystallizes with 1 molecule of water. It decomposes when heated into water and sodium disulphate (p. 167), and the latter compound is converted into normal sodium sulphate and sulphuric anhydride at a higher temperature.

Sodium Sulphite: $SO\begin{cases}ONa\\ONa\end{cases}$ is obtained from the acid salt by adding an equal quantity of sodium carbonate as was used in its preparation; it crystallizes without water from its warm solution, and with 7 molecules in the cold.

Acid Sodium Sulphite: $SO\begin{cases}OH\\ONa\end{cases}$ prepared by saturating a solution of sodium carbonate with sulphurous anhydride. Both salts are easily soluble in water, and both are largely used by brewers for antiseptic purposes—partly to cleanse stale casks, and partly as an addition to the beer to prevent acid fermentation.

Sodium Thiosulphate (*Sodium Hyposulphite*[1]): $SO_2\begin{cases}ONa\\SNa\end{cases} + 5H_2O$, is obtained by evaporating its aqueous solution in large transparent crystals, which melt in their water of crystallization at

[1] See footnote on p. 167.

56°, and lose all their water at 100°. At higher temperatures it is decomposed. Its preparation and its property of dissolving the halogen salts of silver have been already referred to (pp. 168, 169). Large quantities are used for photographic purposes. Owing to its decomposition by chlorine, it is also employed to remove the last traces of chlorine from articles which have been bleached with this substance, and is hence often called an ***antichlor***. A cheap mode of preparing it consists in decomposing a solution of oxidized alkali-waste (p. 169), which contains calcium thiosulphate, with sodium carbonate; insoluble calcium carbonate and a solution of sodium thiosulphate are thus obtained.

Sodium Nitrate (*Chili Saltpetre*): $NO_2 \cdot ONa$, crystallizes in rhombohedra which so closely resemble cubes that it has been called *cubic nitre*. It is more easily soluble in water than potassium nitrate, and only requires about its own weight of water for solution at the ordinary temperature. The salt is found in large deposits in nature, especially in South America on the borders of Chili and Peru, and is an important article of commerce. This crude *nitrate of soda* is, however, far from pure; it contains sodium chloride, iodide and sulphate, together with earthy impurities, and may be purified by crystallization. The mother-liquors are used for the preparation of iodine (p. 124). Pure sodium nitrate may be prepared by neutralizing caustic soda or sodium carbonate with nitric acid.

It has already been mentioned that sodium nitrate is slightly hygroscopic, so that gunpowder prepared from it becomes moist and useless. Nevertheless, sodium nitrate can be readily converted into potassium nitrate, and so used indirectly for the preparation of gunpowder. It is also used for the manufacture of nitric acid.

Sodium Carbonate, or *Soda*: $CO\begin{cases}ONa\\ONa\end{cases} + 10H_2O$.—Just as land-plants require potassium compounds for their growth, so are sodium compounds necessary for sea-plants. The former derive their potash from the soil, the latter obtain their necessary soda from the sea. And when sea-plants are burnt their ashes contain sodium carbonate, in the same way as the ashes of land-plants contain the corresponding potassium carbonate.

Until some eighty or ninety years ago, most of the soda used in the arts was obtained in this way from sea-plants, and, at that time,

large quantities of potash were imported into France and Western Europe from Russia, Germany, and America. But at the end of the preceding century, during the French revolution, this importation of potash into France almost ceased, and many important industries depending upon a supply of alkali seriously diminished. A commission was then appointed by the French Government to examine into any processes for converting common salt into soda, and they decided in favour of the method discovered by *Leblanc*—a process which has remained practically the same from then to the present day. Since then this branch of industry has attained immense dimensions, and the price of soda has fallen so low that in many cases it has displaced the more expensive potash, except when this alkali alone can be used—*e.g.* in the manufacture of potash glass, &c.[1]

The quantity of soda which occurs in the mineral kingdom, partly in the crystalline state and partly in solution, in the soda-lakes of Egypt and North America, is only of local importance, and is inappreciably small in comparison with the immense quantities of this salt which are used for so many purposes.

The conversion of common salt into soda, when casually considered, does not appear a difficult problem. It might be thought that on heating calcium carbonate with sodium chloride the two salts would yield sodium carbonate and calcium chloride. But even supposing this reaction to take place when the dry substances are heated, it would not be possible to separate the sodium carbonate from the calcium chloride, because, on the addition of water, both would be dissolved, and would again produce sodium chloride and insoluble calcium carbonate. Such a process could only be successful if the calcium chloride were converted into a compound insoluble in water. And, as a matter of fact, the process introduced by Leblanc depends upon the conversion of a sodium salt and calcium carbonate into sodium carbonate and an insoluble calcium compound, so that when the mixture is digested with water, sodium carbonate alone dissolves. Leblanc used sodium sulphate for this purpose, and this salt must first be obtained from sodium chloride.

The process of manufacturing soda, or the alkali manufacture, as it is usually called, is not a simple one ; various conditions are necessary for carrying it on successfully, and the process consists of several distinct chemical operations. The manufacture requires,

[1] *See* foot-note on p. 349.

in the first place, a large supply of common salt and limestone, and, secondly, of sulphuric acid. And as the immense quantities of sulphuric acid which are necessary for the production of the sodium sulphate cannot well be obtained from other manufactories, the acid is made on the spot, and sulphuric acid chambers with other requisites for manufacturing the acid are one necessity of every alkali works. This sulphuric acid is then used in the first or *salt-cake process*, to convert the sodium chloride into sodium sulphate or *salt-cake*; large quantities of hydrochloric acid being then obtained as a bye-product (p. 108).

After all the preliminary conditions have been fulfilled which are necessary to obtain the sodium sulphate or salt-cake on a sufficiently large scale, the actual operation of soda manufacture, or the conversion of sodium sulphate into sodium carbonate, can be commenced. But it is not the object of this small text-book to describe all the details of the manufacture of alkali, nor indeed can technical chemistry, as little as practical chemistry, be learnt from books. A number of practical details, often apparently inexplicable, must be attended to if the manufacture is to be a success, and these details cannot be learnt from books, but a knowledge of them must be acquired in the manufactory itself. And this is true not only for the manufacture of soda but also for every other branch of chemical industry. There is always a gap between theoretical and practical chemistry, which remains unbridged for the man who works by rule-of-thumb, but which is readily accounted for by the scientific chemist who has learnt to observe accurately and to solve chemical problems by experiment.

It is therefore sufficient if the student understands the chemical reactions upon which the change of sodium sulphate into sodium carbonate depends.

In the second process of alkali manufacture—the *black-ash process*—the sodium sulphate (salt-cake) is mixed with calcium carbonate (limestone) and small coal, the mixture heated in rotating furnaces, and the black mass (*black-ash*) which remains behind lixiviated with water to dissolve the sodium carbonate. The salt then crystallizes out on evaporating this solution. The chemical reactions which produce this change are as follows. Sodium sulphate, when heated with the carbon of the coal, is converted into sodium sulphide and carbonic oxide :—

$$SO_2(ONa)_2 + 4C = Na_2S + 4CO,$$

and this sodium sulphide is at once decomposed by the calcium carbonate, producing sodium carbonate and calcium sulphide :—

$$Na_2S \quad + \quad CO{\cdot}O_2Ca \quad = \quad CO(ONa)_2 \quad + \quad CaS.$$

On lixiviating this mass with water, the soluble sodium carbonate dissolves, and the insoluble calcium sulphide remains behind. This insoluble residue of impure calcium sulphide constitutes *alkali-waste*, and when exposed to the air, gradually forms poly-sulphides of calcium and other salts which dissolve in the drainage water, and which liberate sulphuretted hydrogen when coming into contact with acid liquors. Hence, not only is the loss of material in the waste very considerable (it contains the whole of the sulphur present in the sulphuric acid employed), but it is also an intolerable nuisance to the neighbourhood of alkali works. Many proposals have been made to recover the sulphur from this waste, some of which have proved partially successful.

In practice, a much larger quantity of limestone is employed than that represented by the above equation. This excess of limestone becomes converted into quick-lime during the heating, and then produces a corresponding quantity of caustic soda, which remains in the mother-liquor after the sodium carbonate has crystallized out. In some alkali works considerable quantities of caustic soda are manufactured in this way.

Soda is also manufactured to some extent from cryolite, a double fluoride of sodium and aluminium : $3NaF, AlF_3$ (p. 134). This compound, when mixed with powdered limestone and strongly heated, decomposes into soluble sodium aluminate and insoluble calcium fluoride :—

$$Na_3AlF_6 \quad + \quad 3CO{\cdot}O_2Ca \quad = \quad Na_3AlO_3 \quad + \quad 3CaF_2 \quad + 3CO_2.$$

And when a stream of carbonic acid is led through the solution of sodium aluminate produced on digesting the mass with water, sodium carbonate is formed and aluminium hydrate precipitated.

The direct conversion of common salt into soda has been very successfully worked in recent years, and the quantity of soda annually produced by this *ammonia-soda process* is rapidly increasing. It has been found that a mixed solution of common salt and acid ammonium carbonate is converted under a pressure of about two atmospheres into ammonium chloride and acid sodium carbonate :—

$$NaCl \quad + \quad CO\begin{cases}OH\\ONH_4\end{cases} \quad = \quad CO\begin{cases}ONa\\OH\end{cases} \quad + \quad NH_4Cl.$$

The process which is based upon this reaction is carried out in the following manner. A saturated solution of common salt is mixed with ammonia, and then saturated with carbonic acid under a pressure of two atmospheres. The acid sodium carbonate, which is only difficultly soluble in water, then separates out, is filtered off under pressure, and converted into the normal carbonate by heating. The carbonic acid which is then given off is again used to reconvert the ammonia which is recovered from the ammonium chloride into ammonium carbonate.

The ammonia-soda process is not only simpler than the older method, but it only yields one bye-product—viz. calcium or magnesium chloride, arising from the decomposition of the ammonium chloride by lime or magnesia. Leblanc's process, on the other hand, gives a number of objectionable residues, from which only a portion of the sulphur can be again obtained. Still the ammonia process can never entirely displace the black-ash process, because we cannot dispense with hydrochloric acid which is produced in such large quantities as a bye-product.

Although the compounds of sodium and potassium as a general rule are very similar to one another, the two carbonates are strikingly different, especially in their behaviour with water. Potassium carbonate is very soluble in water, and can only be obtained in the crystalline form with difficulty; it even attracts moisture from the air and deliquesces. Sodium carbonate, on the other hand, is much less soluble in water, and can be easily obtained in large crystals, which when exposed to the air rapidly lose water and effloresce. A dry fresh crystal placed on the scale-pan of a balance loses weight rapidly and continuously.

The ordinary crystals of sodium carbonate are large transparent monoclinic tablets containing 10 molecules or 63 per cent. of water. When these crystals are heated, they melt at 50° in their water of crystallization, to form a clear liquid. At a higher temperature water is expelled, and finally the anhydrous salt remains behind. Sodium carbonate when crystallized from solutions above 50° contains only 7 molecules of water. The degree of solubility of sodium carbonate in water at different temperatures varies considerably. The solubility increases with the temperature up to about 35°, but then begins to diminish, with the separation of a salt containing less water.

The crystals when exposed to the air become covered with a

thin, loosely attached layer of a compound containing less water, into which the salt is finally completely converted. If a crystal of soda which has been long exposed to the air is broken, a small nucleus of the transparent undecomposed salt may often be found in the centre.

When strongly heated in a platinum crucible, anhydrous sodium carbonate melts to a clear liquid, without undergoing decomposition; carbonic acid is not expelled. An aqueous solution of sodium carbonate, like one of potassium carbonate, reacts strongly alkaline.

Acid Sodium Carbonate: $CO\begin{cases}ONa\\OH\end{cases}$.—This salt, which is commonly known as bicarbonate of soda, is obtained by leading a stream of carbonic acid through a strong solution of the normal carbonate. The acid carbonate, owing to its smaller solubility, then separates out as a crystalline powder. It is usually prepared by saturating a mixture of 1 part of the crystalline normal carbonate and 3 parts of the anhydrous salt with carbonic acid. The salt crystallizes without water in small distorted monoclinic plates, and requires about 11 parts of water for solution at the ordinary temperature. Its solution reacts neutral, but loses carbonic acid when boiled, and is first converted into the so-called *sesquicarbonate of soda*, which is a hydrated double compound of the normal and acid carbonates, of the composition :—

$$CO\begin{cases}ONa\\ONa\end{cases} + 2CO\begin{cases}ONa\\OH\end{cases} + 3H_2O.$$

This double compound is found in nature as small hard crystals, which are permanent in the air. It separates on the banks of the soda-lakes of Egypt and America, and is brought into trade under the name of *Trona*.

Acid sodium carbonate is used to some extent in medicine, especially in the preparation of Seidlitz powders. It is found in many mineral springs, and particularly in those which are alkaline.

Phosphates of Sodium.—Of the various compounds of phosphoric acid and sodium, the best known and most important is

Monacid Sodium Phosphate: $PO\begin{cases}(ONa)_2\\OH\end{cases} + 12H_2O$, which is obtained by nearly neutralizing caustic soda or sodium carbonate with ordinary phosphoric acid. On evaporating this solution down, the

salt separates out in large transparent crystals which easily effloresce in the air. Its solution possesses a faint alkaline reaction although it is an acid salt. The hydrated salt readily loses its 60 per cent. of water of crystallization when heated to 100°; and at a red heat it is decomposed into water and sodium pyrophosphate (p. 219).

Normal Sodium Phosphate: $PO(ONa)_3 + 12H_2O$, crystallizes in thin six-sided prisms when a solution of the preceding salt is mixed with sufficient caustic soda and evaporated down. The solution has a strong alkaline reaction; it absorbs carbonic acid from the air, and becomes converted into sodium carbonate and the monacid phosphate.

Diacid Sodium Phosphate: $PO\left\{\begin{matrix}ONa\\(OH)_2\end{matrix}\right. + H_2O$, is obtained when a solution of the monacid phosphate is mixed with as much phosphoric acid as it already contains. The solution has an acid reaction; when evaporated down it yields the salt in rhombic prisms, which are easily soluble in water.

Very different from these three salts is the sodium compound of monobasic metaphosphoric acid:

Sodium Metaphosphate: $PO_2 \cdot ONa$, which is obtained by heating diacid sodium phosphate:—

$$PO\left\{\begin{matrix}ONa\\(OH)_2\end{matrix}\right. = PO_2 \cdot ONa + H_2O$$

(p. 219), as an amorphous vitreous mass, and which cannot be obtained in the crystalline form.

Sodium Pyrophosphate: $O\left\{\begin{matrix}PO(ONa)_2\\PO(ONa)_2\end{matrix}\right. + 10H_2O$, is prepared by heating the monacid sodium phosphate to redness (p. 219), and separates from an aqueous solution of the residue in large crystals, which are permanent in the air. Its solution may be boiled without change, but if nitric acid is added and the solution then boiled, the salt is decomposed into sodium nitrate and diacid sodium phosphate.

Sodium Arsenate: $AsO\left\{\begin{matrix}(ONa)_2\\OH\end{matrix}\right. + 12H_2O$, which is isomorphous with the corresponding common sodium phosphate, is deposited from its aqueous solution in large well-developed crystals. It is largely used in calico-printing and dyeing. The *normal* and *diacid arsenates* closely resemble the corresponding phosphates.

Sodium Borate : $B_4O_5(ONa)_2 + 10H_2O$ (p. 264).—This salt, which is commonly known as *borax*, and is found in nature as the mineral *tinkal*, is prepared by neutralizing a hot solution of sodium carbonate with boric acid. When the solution is allowed to evaporate slowly the salt separates out as large transparent monoclinic prisms of the above composition, which only slightly change in the air. At the ordinary temperature 100 parts of water only dissolve about 7 parts of the salt, but the same quantity of water dissolves more than 200 parts of the salt at 100°. The solution possesses a faint alkaline reaction. From a concentrated aqueous solution of borax at 70° or 80°, the salt crystallizes in octahedra with only 5 molecules of water. This *octahedral borax* is distinguished from ordinary prismatic borax by its greater hardness. Borax loses its water when heated and swells up into a porous mass; at higher temperatures the salt melts to a clear liquid which solidifies on cooling to a hard transparent glass. Fused borax possesses the property of dissolving metallic oxides, often in considerable quantities, and the variously coloured glasses which are thus produced afford a test for various metals. Thus cobalt oxide imparts a blue colour to fused borax; manganic oxide gives a violet, but manganous oxide a colourless glass; while cupric oxide and chromic oxide yield green-coloured glasses.

Borax is employed in the arts as well as in the laboratory. Its property of dissolving metallic oxides makes it useful in soldering two pieces of metal together when the surfaces to be united must be perfectly free from oxide. Considerable quantities of borax are used for glazing porcelain and in the manufacture of enamels. It is also a valuable medicine.

The compounds of sodium with the halogens and with sulphur closely resemble the corresponding compounds of potassium, and of these the chloride is the only one which need be referred to in detail.

Sodium Chloride (*Common Salt*) : NaCl.—This salt not only occurs widely distributed in nature, but is also found in immense quantities, partly as solid *rock-salt*, and partly in aqueous solution in brine springs and in the sea.

Common salt crystallizes in the regular system, and generally in cubes. It contains no water of crystallization, but usually includes small quantities of water mechanically, which cause the

crystals to decrepitate when heated. It possesses a well-known saline taste, and is only slightly more soluble in hot than in cold water. 100 parts of water dissolve 36 parts of salt at the ordinary temperature, and only 39 parts at 100°. The concentrated aqueous solution, therefore, scarcely contains 27 per cent. of the salt. It is insoluble in strong alcohol. When an aqueous solution of common salt is evaporated down, the crystallization commences first where the concentration is greatest—*i.e.* on the surface—and the small cubes which are thus produced gradually increase in weight, and sink to the bottom of the vessel.

The extraction of salt from the brine springs of Cheshire and Worcestershire is an extremely simple process, and consists in evaporating the brine in shallow iron pans. In countries where fuel is dear and the brine less concentrated—*e.g.* in Germany, the solution is allowed to trickle several times over tall walls of faggots of thorn, which exposes a large surface to the air, and causes a rapid evaporation of water. After a concentrated solution has been obtained by this process (called *graduation*), the strong brine is boiled down in iron pans.

In the same way, salt has also been obtained from sea-water, although this liquid only contains about 3·5 per cent. of it. In warm southern climates, for example, in the south of France and on the coast of Africa, shallow basins are filled by the sea at high water, then closed, and the water evaporated by the heat of the sun and by the warm winds. Salt obtained from sea-water in its crude state, and containing various impurities, is commonly known as *bay-salt.*

Brine springs are produced by water coming into contact with deposits of rock-salt in the earth, and artificial springs are very often formed by drilling down to the layer of salt and pumping in water. In some cases the rock-salt is mined in the ordinary way, and brought to the surface in the solid state. The chief deposits of salt occur in Galicia, in various parts of Germany, and at Northwich and Droitwich in England. Very important salt deposits have been recently discovered at Stassfurt, near Magdeburg, where the common salt is associated with potassium chloride and other compounds.

Rock-salt can be used in its crude state for most technical purposes, but not as a condiment, as it possesses an impure taste due to various impurities, which may, however, be separated from it by recrystallizing it from its solution in water.

Commercial common salt often differs both in its external appearance and in its taste. In some cases the cubes in which it crystallizes are arranged together in large pyramids, in other cases they are separate and form a granular crystalline powder. One sample may become moist in the air, and possess an intense saline taste, while another remains dry, and tastes much less salt. The form in which the salt crystallizes depends partly on the temperature of evaporation, and partly upon the presence or absence of foreign substances, such as sodium sulphate, magnesium chloride, or calcium chloride. The two latter salts are those which cause the salt to deliquesce in the air, and which impart the sharp saline taste that some samples possess. Pure sodium chloride does not become moist when exposed to the air, and has a pure saline taste.

Common salt is almost as essential for the life and health of men and animals as the air which they breathe, and if a State imposes a tax upon this most necessary food (as in Germany), while luxuries such as tobacco remain almost untaxed, it proves that its rulers lack scientific training, and that they do not understand the simplest and most important questions bearing upon the material well-being of the people.

Detection of Sodium Compounds.

The intensely yellow colour which sodium compounds impart to a Bunsen flame, and the single yellow line (see App.) of the sodium spectrum (see table of spectra), are so characteristic that it is scarcely possible to overlook the presence of even small quantities of the metal. Sodium salts may be distinguished from those of potassium by the solubility of sodium chlorplatinate: Na_2PtCl_6, both in water and in alcohol. The two carbonates are also very different. Potassium carbonate deliquesces in the air, but the sodium salt effloresces.

LITHIUM.

Chemical Symbol: Li.—*Atomic Weight*: 7.

Lithium is a rare element, but on account of the extensive use of some of its compounds in medicine is of considerable value. It

is also widely distributed in nature, and is found, though always in small quantities, in the minerals: *lepidolite*, *petallite*, *triphylline*, &c., as well as in numerous mineral springs, especially in one near Redruth in Cornwall.

The solubility of lithium carbonate in water affords a basis for the separation of this salt from the carbonates of the alkaline earths, while, on the other hand, its nearly insoluble phosphate permits its separation from the easily soluble phosphates of the alkalies. The preparation and purification of lithium compounds depend on the properties of these two salts.

Metallic lithium, which may be prepared by electrolysis of its fused chloride, is a silver-white tough metal, harder than potassium or sodium, but softer than lead. It is distinguished by its low specific gravity (0·59), and is, in fact, the lightest solid known. Its melting-point is 180°, but, unlike potassium and sodium, it is not volatile at a red-heat, and can only be distilled at very high temperatures. In the air it oxidizes less easily than potassium and sodium, but its freshly-cut surface soon becomes covered with a coating of oxide. When heated in the air above its melting-point, it catches fire and burns brightly. Water is easily decomposed by it at the ordinary temperature, but the hydrogen is not inflamed. It burns readily in chlorine, producing its chloride.

Of the compounds of lithium: *lithium oxide* and *lithium peroxide* have been but little investigated.

Lithium Hydrate (*Lithia*): $LiOH$, which may be prepared by boiling the carbonate with slaked-lime, remains behind on evaporating the alkaline solution in a silver dish as a white, transparent, easily fusible mass. It resembles caustic soda in external appearance, but is less soluble in water and does not deliquesce in the air.

Lithium Sulphate: $SO_2\left\{\begin{matrix}OLi\\OLi\end{matrix}\right. + H_2O$, crystallizes in rhombic prisms and is easily soluble in water.—*Lithium Nitrate*: $NO_2 \cdot OLi$, crystallizing without water in rhombohedra, is very easily soluble in water, and deliquesces in moist air.

Lithium Phosphate: $2PO(OLi)_3 + H_2O$, is very difficultly soluble in water, and is precipitated on mixing a solution of monacid sodium phosphate with one of a soluble lithium salt as a white, heavy crystalline powder, the quantity of which is increased

on neutralizing the liquid with a little caustic soda or ammonia. The salt requires about 2,500 parts of water for its solution at the ordinary temperature, and is still less soluble in water containing ammonia.

Lithium Carbonate: $CO\begin{cases}OLi\\OLi\end{cases}$.—This compound, which is also difficultly soluble in water in comparison with the carbonates of potassium and sodium, is deposited as a white powder on adding sodium carbonate to a concentrated solution of lithium chloride. It dissolves in about 100 parts of water at the ordinary temperature, yielding a solution which is faintly alkaline. Hot water dissolves less, and it is insoluble in alcohol. Lithium carbonate possesses the remarkable property of forming a soluble compound with the insoluble uric acid, and is therefore largely taken as a medicine to remove this substance from the body, when it separates out during the progress of certain diseases (gouty affections, stone, &c.). The lithium carbonate is usually given in water containing free carbonic acid (lithia-water), in which the salt dissolves more readily than in pure water.

Lithium Chloride: $LiCl$, crystallizes from very concentrated solutions in cubes or octahedra. It is very soluble in water and deliquesces in the air. It is also soluble in alcohol, and even in a mixture of alcohol and ether. When fused in an open vessel it loses some chlorine and becomes partially converted into a basic chloride.

Detection of Lithium Compounds.

The smallest quantity of a lithium compound gives to a non-luminous gas flame a splendid crimson colour. The spectrum consists of a bright red and a faint orange line. The precipitates produced by sodium carbonate or phosphate in strong solutions of lithium compounds also serve to distinguish them from those of potassium and sodium.

RUBIDIUM AND CÆSIUM.

Chemical Symbols: $\begin{cases}Rb\\Cs\end{cases}$.—*Atomic Weights*: $\begin{cases}85{\cdot}4\\132{\cdot}9\end{cases}$

These two rare elements are as yet only of chemical interest. Both were discovered by Bunsen and Kirchhoff during their

researches in spectrum analysis. The two metals are found in minute quantities in certain minerals, in the ashes of some plants, and in some mineral springs. One of the richest sources of the two chlorides is the mineral water of Dürkheim in the Bavarian Palatinate, in which cæsium was first discovered by Bunsen, but even this only contains one part of cæsium chloride in 6,000,000 parts of the water.

Rubidium, which is obtained, like potassium and sodium, by glowing an intimate mixture of its carbonate and charcoal, is a white metal with a faint yellowish tint. It is as soft as wax even at 10°, melts at 38°, and has a specific gravity of 1·5. It at once oxidizes when exposed to the air, and then becomes so strongly heated that it soon catches fire. When brought into contact with water, decomposition at once takes place and the liberated hydrogen is ignited.

The compounds of rubidium so closely resemble those of potassium that it is very difficult to separate the two from one another. The double chlorides of the metals with platinum are best adapted for this separation, the rubidium compound ($2RbCl, PtCl_4$) being much less soluble in water than the corresponding potassium compound. Rubidium is more electro-positive than potassium. Compounds of rubidium when held on a platinum wire in a non-luminous gas flame impart a violet colour to it resembling that of potassium compounds. The spectrum of this flame is, however, quite different, and is characterized by two lines in the red and two in the violet.

Cæsium, which is even rarer than rubidium, has been recently obtained in the metallic state by the electrolysis of a mixture of cæsium and barium cyanides. It is a white, very soft metal, melting at 27° or a summer temperature, and of 1·88 specific gravity. It decomposes water with explosive violence, and is even more electro-positive than rubidium. Cæsium is, therefore, the most electro-positive of all metals, and has a stronger affinity for oxygen, chlorine, &c., than any other metal. Its compounds closely resemble those of rubidium and potassium. In order to separate it from these two metals the solubility of its carbonate in absolute alcohol, in which the carbonates of rubidium and potassium do not dissolve, may be made use of. The spectrum of cæsium compounds is especially characterized by two lines in the bright blue.

AMMONIUM.

It has already been remarked (p. 188) that we are not acquainted with the substance called ammonium in the free state; but the fact that it forms an amalgam with mercury, and the close relation of its compounds to those of potassium, justify us in deciding in favour of its metallic nature, and in placing it together with the metals of the alkalies. Its composition is expressed by the formula: NH_4, or perhaps more correctly as $N_2H_8 = (NH_4)_2$.

Ammonium oxide and hydrate are just as little known as ammonium itself; but it is extremely probable that the aqueous solution of ammonia contains the latter compound: $NH_3 + H_2O = NH_4OH$, but this can no more be proved than the assertion that a solution of carbonic anhydride in water contains carbonic acid: $CO\left\{\begin{matrix}OH\\OH\end{matrix}\right.$. The facts that compounds of the type NR'_4OH, where R' represents a monovalent organic radical, and which resemble the solution of ammonia in many properties, exist, and that no compound of the type NR'_5O can be obtained, are best explained on this hypothesis.

The ammonium salts are easily obtained by neutralizing ammonia or ammonium carbonate with the corresponding acid. Like those of potassium, they are nearly all soluble in water, and mostly crystallize well. (See Appendix.)

Ammonium Sulphate: $SO_2\left\{\begin{matrix}ONH_4\\ONH_4\end{matrix}\right.$.—This salt, which is isomorphous with potassium sulphate, can easily be obtained in the crystalline state. It melts at 140°, and decomposes at higher temperatures into ammonia, water, nitrogen, and a sublimate of hydrogen ammonium sulphate. It is manufactured on a large scale by leading the ammonia evolved on heating the ammoniacal-liquor of the gas works with milk of lime into dilute sulphuric acid until saturation, and then evaporating down. The hydrogen salt, mentioned above, has the composition: $SO_2\left\{\begin{matrix}OH\\ONH_4\end{matrix}\right.$. Besides these compounds, normal salts, in which one of the atoms of ammonium in ammonium sulphate is displaced by potassium or sodium, also

exist; they have the composition: $SO_2\left\{\begin{matrix}OK\\ONH_4\end{matrix}\right.$ and $SO_2\left\{\begin{matrix}ONa\\ONH_4\end{matrix}\right.$ $+ 2H_2O$.[1]

Ammonium Nitrate: $NO_2\cdot ONH_4$, crystallizes in six-sided prisms, without water, and is isomorphous with potassium nitrate. It is easily soluble in water, absorbing heat, and deliquesces in the air. When heated it first melts and is then converted into nitrous oxide and water (p. 198).

Ammonium Phosphates.—The compounds of phosphoric acid with ammonia closely resemble those of sodium and potassium. A salt corresponding to the monacid phosphate: $PO\left\{\begin{matrix}(ONH_4)_2\\OH\end{matrix}\right.$ in which one atom of ammonium is displaced by one of sodium, is the compound called *microcosmic salt*, or monacid sodium-ammonium phosphate: $PO\left\{\begin{matrix}OH\\ONH_4\\ONa\end{matrix}\right. + 4H_2O$. It is easily obtained by dissolving 6 or 7 parts of common sodium phosphate and 1 part of ammonium chloride in 2 parts of boiling water, and separates out on cooling in well-defined crystals. It may be freed from the sodium chloride which it contains by recrystallizing with the addition of a little ammonia.

This salt loses its water when heated, and then gives off ammonia, leaving sodium metaphosphate: $PO_2\cdot ONa$, as an easily fusible mass. For this reason the salt is used in blowpipe analysis. A fragment heated on a platinum wire in a Bunsen burner gives a glass bead of sodium metaphosphate, which, like borax, can dissolve various metallic oxides and become coloured by them. Silica is not dissolved by the fused salt, and may thus be readily detected.

Ammonium Carbonate.—On the union of ammonia and carbonic acid, different compounds are produced according to the conditions under which the combination takes place. It has already been stated (p. 290) that if the two gases act upon one another in the absence of water, *ammonium carbamate*: $CO\left\{\begin{matrix}NH_2\\ONH_4\end{matrix}\right.$

[1] These may also be regarded as double salts of the two sulphates, thus:—
$SO_2\left\{\begin{matrix}OK\\OK\end{matrix}\right. + SO_2\left\{\begin{matrix}ONH_4\\ONH_4\end{matrix}\right.$ and $SO_2\left\{\begin{matrix}ONa\\ONa\end{matrix}\right. + SO_2\left\{\begin{matrix}ONH_4\\ONH_4\end{matrix}\right. + 4H_2O$, but are best represented by the above formulæ.—ED.

and not ammonium carbonate is formed. The same salt is also produced when aqueous ammonia is saturated with carbonic acid, although the chief product of this reaction is ammonium carbonate. And it is highly probable that the normal as well as the acid salt which crystallize from concentrated solutions (the former when ammonia is in excess, the latter with excess of carbonic acid) contain ammonium carbamate.

The commercial ammonium carbonate (*carbonate of ammonia*) is manufactured by heating a mixture of ammonium chloride or sulphate with powdered chalk; it then sublimes as a translucent, crystalline solid, with a strong ammoniacal odour. When exposed to the air, it crumbles to a white crystalline powder, consisting chiefly of acid ammonium carbonate. This substance was previously thought to be a mixture of the normal and acid ammonium carbonates, of the composition: $CO\begin{cases}ONH_4\\ONH_4\end{cases} + CO\begin{cases}OH\\ONH_4\end{cases}$ hence its old name of sesquicarbonate, but is now known to contain considerable quantities of ammonium carbamate, and is therefore a mixture of several salts. The presence of the ammonium carbamate may be readily shown by shaking the freshly prepared solution with calcium chloride, and filtering off the clear solution from the precipitated calcium carbonate. This solution contains calcium carbamate, which gradually decomposes on standing, more quickly if heated, with the formation of insoluble calcium carbonate. A solution of ammonium carbonate free from the carbamate does not give the same result; nor does a solution of the commercial salt which has been prepared for some time, since ammonium carbamate when dissolved in water gradually, or quickly if warmed, takes up the elements of water, and becomes converted into ammonium carbonate.

Ammonium carbonate is produced during the destructive distillation of nitrogenous organic substance—*e.g.* coal. And although the quantity of nitrogen contained in coal is very small, and only a part of this nitrogen is converted into ammonia, still the immense quantities of coal which are used for the manufacture of coal-gas are so great that very nearly all the ammonium compounds now brought into trade are derived from the ammoniacal liquors of the gas-works.

Ammonium carbonate is also produced by the putrefaction of organic compounds containing nitrogen. Large quantities are always present in putrid urine and sewage, and are produced from

the decomposition of the urea which they contain. This compound takes up two molecules of water during putrefaction, and becomes converted into ammonium carbonate :—

$$\underset{\text{Urea}}{CH_4N_2O} + 2H_2O = CO\begin{cases} ONH_4 \\ ONH_4 \end{cases}$$

Ammonium Chloride (*Sal-ammoniac*): NH_4Cl.—This salt is brought into trade in two forms. First, when crystallized from water as a white powder of small octahedra, or cubes, grouped together; and secondly, when obtained by sublimation as a fibrous, crystalline, and compact mass. It possesses a saline taste, and is soluble in about 2·5 parts of water at the ordinary temperature, or in rather more than its own weight at 100°. It is nearly insoluble in alcohol. When heated it volatilizes, without melting, and undergoes partial decomposition. At 350° the dissociation into hydrochloric acid and ammonia is complete, though these substances reunite on cooling.

In former times large quantities of sal-ammoniac were imported from Egypt, where, for lack of other fuel, dried camel's dung was burnt. The nitrogen and common salt contained in the dung gave rise on burning to ammonium chloride, which was deposited with the soot in the chimneys, and was afterwards purified by some crude method.

Beautiful crystals of ammonium chloride are sometimes found in the cavities of solidified lava, and it was formerly thought that the salt had been sublimed with the lava from the interior of the earth. But it has been proved by Bunsen, from observations of volcanic phenomena in Iceland, that crystals of ammonium chloride are only found where the glowing lava has flowed over ground covered with vegetation. The ammonia produced by the dry distillation of the plants would then unite with the free hydrochloric acid contained in the lava, and so produce ammonium chloride.

Ammonium chloride, like all other ammonium compounds, is now almost exclusively obtained from the ammoniacal liquor of the gas-works (p. 322). The ammonia which is evolved on heating the gas-liquor with milk of lime is passed into dilute hydrochloric acid until saturated, and the solution so obtained then evaporated down. The crude salt is afterwards purified, either by crystallization or by sublimation.

Sal-ammoniac is largely used in the arts for the preparation of ammonia (p. 184), as a valuable medicine, in dyeing, and for many other purposes.

Ammonium Bromide: NH_4Br, closely resembles the chloride, but is still more soluble in water. It is largely used in photography and in medicine.

Ammonium Sulphide: $(NH_4)_2S$, and **Ammonium Sulphydrate**: $(NH_4)HS$.—Both compounds may be obtained in the crystalline form by allowing dry ammonia and dry sulphuretted hydrogen to act upon one another. To obtain the former, ammonia and sulphuretted hydrogen are mixed at $-18°$, in the proportion by volume of two to one. To prepare the hydrogen salt the two gases are mixed in equal volumes at the ordinary temperature. Ammonium sulphydrate may also be prepared by leading sulphuretted hydrogen into a saturated solution of ammonia in absolute alcohol, when the compound crystallizes out. The two compounds are usually prepared in aqueous solution. If aqueous ammonia is completely saturated with sulphuretted hydrogen, ammonium sulphydrate is formed, and if to this liquid the same quantity of ammonia is added as was used for its preparation, it is converted into ammonium sulphide.

Both are colourless liquids, soon becoming yellow when exposed to the air, and smelling both of ammonia and sulphuretted hydrogen. The yellow colour which the solutions acquire when exposed to the air is due to partial oxidation of the sulphuretted hydrogen which they contain. During this process water and free sulphur are produced, and the latter substance then dissolves in the undecomposed sulphide. Ammonium sulphide, like potassium sulphide, can dissolve large quantities of sulphur, and so produce polysulphides corresponding to those of potassium.

Ammonium sulphide is much used in analytical chemistry, partly to precipitate the sulphides of those metals which are insoluble in water, but which are not formed by the action of sulphuretted hydrogen on an acid solution, and partly to dissolve those insoluble sulphides which have the character of sulpho-acids (*e.g.* antimony sulphide). With such sulphides it forms soluble sulphosalts, and they may be thus separated from other insoluble sulphides (*e.g.* lead sulphide) which have not this property.

Oxyammonium Salts.—Just as ammonia unites with acids and forms the ammonium salts, in the same manner the derivative of ammonia—oxyammonia or hydroxylamine: $NH_2 \cdot OH$ (p. 186)—

produces with acids the salts of the radical oxyammonium. The radical itself: NH_3OH or $(NH_3OH)_2$, is as little known in the free state as is ammonium. (See Appendix.)

Oxyammonium Sulphate: $SO_2\left\{\begin{matrix}O(NH_3OH)\\O(NH_3OH)\end{matrix}\right.$ crystallizes from its aqueous solution in large colourless prisms, and is insoluble in alcohol.

Oxyammonium Chloride: $NH_3OH\cdot Cl$, is soluble both in water and in absolute alcohol, and by this latter property can be separated from ammonium chloride. It crystallizes from water in tablets, from alcohol in monoclinic prisms, melts at 100°, and is decomposed at a slightly higher temperature into nitrogen, hydrochloric acid, ammonium chloride, and water.

Detection of Ammonium Compounds.

The similarity between the ammonium and potassium compounds is so close that on mixing solutions of ammonium chloride and platinum chloride a yellow crystalline precipitate of ammonium chlorplatinate: $(NH_4)_2PtCl_6$, is produced, just as difficultly soluble in water, and just as insoluble in alcohol as the potassium compound. If, however, the ammonium compound is heated, ammonium chloride and chlorine are evolved, and pure spongy platinum remains behind, from which water extracts nothing.

Compounds of ammonium are best recognized by their behaviour with caustic alkalies (potash, soda, or lime), which liberate ammonia even in the cold, but more readily when gently warmed. This free ammonia can be detected by its odour, and by the white fumes of ammonium chloride produced when a glass rod, moistened with hydrochloric acid, is brought near the liquid.

Minute traces of free ammonia or ammonium compounds may be detected by *Nessler's solution*—an alkaline solution of potassium-mercuric iodide. When a few drops of this solution are added to a dilute solution containing ammonia or a salt of ammonium, a reddish-brown precipitate or corresponding colour is at once produced. In this way it is possible to detect $\frac{1}{300}$ of a milligramme of ammonium chloride dissolved in 50 c.c. of water.[1]

[1] See Appendix.

METALS OF THE ALKALINE EARTHS.

The five metals belonging to this group—*calcium*, *strontium*, *barium*, *magnesium*, and *beryllium*—are distinguished from the metals of the alkalies by their weaker attraction for oxygen, and further by the fact that their oxides, or rather hydrates, are much less soluble than those of the alkali-metals, and do not deliquesce in the air. Their sulphates (except those of magnesium and of beryllium) are also much less soluble in water than the alkaline sulphates, and their carbonates are quite insoluble. They are all diads in most of their compounds.

By far the most important of this group of metals is calcium, the one we have placed first.

CALCIUM.

Chemical Symbol: Ca.—*Atomic Weight*: 40·1.

Calcium, with oxygen, silicon, and aluminium, belongs to those elements which are most widely distributed in nature. It is never found in the metallic state, but usually in combination with oxygen as some salt, never as the free oxide. In combination with fluorine it forms the important mineral *fluor-spar*, and occurs as its chloride in many mineral waters and in the sea.

The most important oxygen compounds of calcium found in nature are the very various forms of its carbonate, its sulphate (as *gypsum*), its phosphate, and its silicate, which is a constituent of many rocks.

Metallic calcium, which is difficult to prepare pure, is only of theoretical interest. It may be obtained by heating calcium iodide with sodium in a well-closed iron crucible, or by heating a mixture of 3 parts of calcium chloride, 4 parts of zinc, and 1 part of sodium in a Hessian crucible. An alloy of zinc and calcium is thus obtained, from which the zinc may be volatilized by strong heating in a crucible of gas-carbon, placed inside a larger one of clay, then leaving a regulus of metallic calcium behind. The best method of all of obtaining pure calcium is by the electrolysis of its fused chloride.

Calcium is a brilliant pale yellow metal, of about the same hard-

ness as lead. Its specific gravity is 1·6; it is malleable, but becomes brittle when hammered. When exposed to moist air, calcium soon becomes covered with a grey coating of oxide and is gradually converted into calcium hydrate. It decomposes water at the ordinary temperature, but the hydrogen does not catch fire. The metal burns brilliantly when heated to redness in the air, or in chlorine. Dilute nitric acid acts violently on it, but the concentrated acid does not attack it.

Calcium, like the other metals of the group, is nearly always a diad element; it may possess a valency of four in the peroxide, and possibly also in bleaching-powder.

Calcium Oxide, *Quick-lime*: CaO.—This oxide can be far more easily obtained than the oxide of potassium or sodium. It suffices to heat the carbonate strongly in the air in order to expel the whole of the carbonic acid, and leave the oxide behind. The product so obtained is then more or less pure according to the purity of the material used for its preparation. Crystallized calcite, especially transparent Iceland-spar, yields oxide chemically pure, and white marble nearly so.

It is remarkable that calcium carbonate is only completely decomposed by heating when a second indifferent gas is present. If heated in an atmosphere of carbonic acid, decomposition goes on until a certain pressure (depending on the temperature) is reached, and then ceases. Marble or Iceland-spar when heated in a closed crucible is only partially decomposed, because it is always surrounded with an atmosphere of carbonic acid. Complete decomposition can, however, be easily brought about by placing a piece of charcoal on the bottom of the crucible. The glowing charcoal then converts the carbonic acid into carbonic oxide, into which the former gas can diffuse until all the calcium carbonate is decomposed.

Calcium oxide or quick-lime is a white amorphous mass, usually retaining the form of the calcium carbonate from which it has been prepared. It is infusible, even in the oxy-hydrogen blowpipe, but becomes then so strongly heated as to emit a most intense white light (lime-light). When exposed to the air, it absorbs water and carbonic acid, and crumbles to a fine white powder, which effervesces with hydrochloric acid.

If water is poured on to quick-lime, the porous mass first absorbs considerable quantities of the liquid like a sponge. After a short

time chemical action sets in, and the calcium oxide unites with water to form calcium hydrate :—

$$CaO + H_2O = Ca(OH)_2.$$

The reaction is accompanied with so large an evolution of heat that a portion of the water is converted into steam. At the same time the piece of quick-lime swells up and is finally converted into a dry, white, soft powder of the following compound, calcium hydrate.

Calcium Hydrate, *Slaked-lime* : $Ca\begin{cases}OH\\OH\end{cases}$—This hydrate is slightly soluble in water, 1 part requiring 600 parts of cold water to dissolve it. In hot water it is less soluble than in cold, whence it follows that a cold saturated solution when boiled becomes turbid, and calcium hydrate separates in the crystalline form, but redissolves as the solution again cools. The solution has a distinct alkaline reaction.

Slaked-lime mixed with water forms a turbid solution of the hydrate with undissolved suspended particles. Such a mixture is called *milk of lime*. If this is filtered, the suspended particles remain behind on the filter, and clear alkaline *lime-water* runs through. Lime-water must be preserved in well-stoppered bottles, as it absorbs carbonic acid from the air and becomes turbid from the insoluble calcium carbonate so produced. This property of lime-water makes it useful for detecting carbonic acid, even when mixed with large quantities of other gases—*e.g.* in coal-gas.

Calcium hydrate easily loses its water when heated to redness —more easily than calcium carbonate parts with its carbonic acid— and is reconverted into calcium oxide.

Slaked-lime is largely employed for numerous and highly important technical purposes. Immense quantities are used for the preparation of *mortar*. For this purpose it has been employed for thousands of years, and it may probably be considered as one of the first chemical compounds artificially prepared by man. It would be interesting to know how and when the knowledge was acquired that limestone, when heated to redness, becomes changed into a new substance, and that this quick-lime when made into a paste with water gradually hardens in the air, or if placed between stones, cements them together. But questions of this nature must, for the present, remain unanswered, since the preparation of mortar from lime was known even in pre-historic times.

Ordinary *mortar* is prepared by mixing slaked-lime and sand together with water to form a paste, which is spread between the bricks or stones to be cemented together. The hardening of the mortar only takes place slowly in the course of years—many years if the walls are thick, and is the more complete the older the walls. And not only does the mortar itself gradually become hard, but it also attaches itself firmly to the stones between which it is placed, and it often happens when old buildings are pulled down that the stones themselves break more easily than the mortar which holds them together. The same effect may be noticed in some of the calcareous conglomerates or pudding-stones, which often consist of quartz pebbles cemented together with limestone, and which if broken by the blow of a hammer usually fracture across the pebbles and not at the joints.

The hardening of mortar is due to the action of the carbonic acid of the air, which gradually unites with the calcium hydrate to form calcium carbonate, while water is expelled :—

$$Ca\begin{cases}OH\\OH\end{cases} + CO_2 = CO\cdot O_2Ca + H_2O.$$

The sand, which the mortar also contains, serves to make the mass more porous, so that the carbonic acid can penetrate into the interior of the walls; it also causes the mortar to adhere more firmly to the bricks or stones. That old buildings—*e.g.* those of the Romans or of the Middle Ages—possess greater solidity than our modern structures is not only because a better kind of mortar was used, but is a natural consequence of the longer action of the carbonic acid. A mortar which has only been exposed to the air for a few years, and which still contains unchanged calcium hydrate, is of course less hard than one on which the carbonic acid has acted for centuries, and in which the whole of the calcium hydrate has been converted into calcium carbonate.

It is considered unhealthy to live, and especially to sleep in the rooms of newly built houses, because the moisture which is contained in the walls continually saturates the air of the rooms. The water mechanically mixed with the mortar soon evaporates from the porous walls, but the walls still remain moist from the water which is gradually set free *chemically* during the union of the calcium hydrate with carbonic acid. The hardening of the mortar, and consequent drying of the walls, can be accelerated by burning coke or charcoal in open grates in the closed rooms. The

large quantities of carbonic acid so produced then quickly penetrate into the walls, and the water which is set free is evaporated by the heat; and to allow this water vapour to escape, it is necessary to open the doors and windows occasionally. In this way the walls of new buildings may be dried in as many hours as they would otherwise require weeks or even months.

The manufacture of the large quantities of quick-lime which are used for the preparation of mortar is carried on in furnaces specially constructed for the purpose—called *lime-kilns*. Two forms of these kilns are shown in figs. 61 and 62. Both are built of firebricks in the form shown. In the one kiln (fig. 61), which is but little used, large pieces of limestone are built below in the

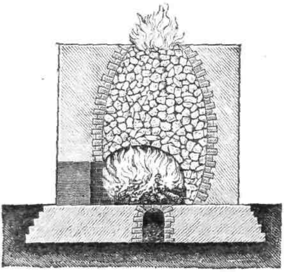


Fig. 61.

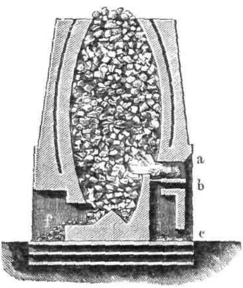


Fig. 62.

form of an arch, and the whole kiln filled up with the same material, leaving free spaces for the hot gases to pass through the entire mass. A fire is then made in the arch below, and continued until the whole of the limestone has been converted into quick-lime. After cooling, the lime is extracted, and the process repeated. Fig. 62 represents a much more economical form, as it is continuous in its action. The kiln is filled with pieces of limestone, and a fire kept up continuously at the side, *a*. The lime is raked out from the bottom of the kiln as it is produced, and fresh limestone introduced at the top to supply its place. A form of kiln largely used in England is similar in shape to fig. 62, but without a side opening for the fire. The kiln is filled with alternate layers of limestone and small coal, and the lowest layer of coal ignited.

As the coal gradually burns away, the lime is abstracted from the base, and fresh alternate layers of limestone and coal are introduced from the top.

Some varieties of limestone contain other compounds than calcium carbonate, such as magnesium carbonate, alumina, and silica. If these are burnt, a lime is obtained which only becomes slightly heated when slaked, and which is unsuitable for the preparation of ordinary mortar. In the case of an argillaceous limestone—*i.e.* one mixed with clay (aluminium silicate), the lime decomposes some of the clay when moistened with water, producing compounds of lime and alumina and of lime and silica, which are insoluble in water, and which, in contact with water, gradually become hard and solid. If such an argillaceous limestone or a mixture of limestone and clay is burnt, then powdered and mixed with water, it gradually hardens, owing to the formation of these insoluble compounds, and becomes harder and harder the longer it remains in contact with water. Mortars of this description, known as *hydraulic mortars*, are therefore especially suited for buildings which are always covered with water.

Hydraulic mortars are prepared from various materials and in varying proportions—some hardening slowly and some quickly. The rapidity with which the mortar hardens depends upon the proportion of clay present: thus *Roman cement,* containing about 30 per cent. of clay, hardens in a few hours; while *Portland cement*, largely made in England by mixing chalk with clay and then carefully burning, contains less clay and hardens more slowly. A hydraulic mortar may also be prepared by mixing quick-lime with soluble silicic acid or with an aluminium silicate which has been acted on by hydrochloric acid; such a silicate is decomposed by the lime in the presence of water.

Calcium hydrate is also used for a large number of other technical purposes—for example, for the preparation of ammonia from ammonium chloride, for the manufacture of the caustic alkalies and of bleaching powder, for the saponification of fats, for the purification of coal-gas, and the manufacture of hard glass, in tanning to remove hair from the skins, &c.

Besides calcium oxide, a second, far less important oxygen compound of calcium is known, viz.:—

Calcium peroxide: CaO_2, which cannot, like barium peroxide, be prepared by heating calcium oxide in oxygen. It is, however,

easily obtained by adding hydrogen peroxide to lime-water, when it is precipitated in crystalline plates. When gently heated it readily loses one-half of its oxygen.

Of the other compounds of calcium, the following are of most general and chemical importance.

Calcium Sulphate: $SO_2 \cdot O_2Ca$.—This slightly soluble salt is largely distributed in nature in different forms, and usually accompanies common salt. The anhydrous compound, of the above composition, is known as *anhydrite*, and occurs either in crystals belonging to the rhombic system or more generally in granular or fibrous crystalline masses.

Far commoner than this is the compound of calcium sulphate with two molecules of water: $SO_2 \cdot O_2Ca + 2H_2O$, which in its most general form is called *gypsum*. This compound is found in nature in very various modifications, but usually as a compact crystalline mass, generally of a greyish colour: gypsum proper or *common gypsum*. Colourless, transparent crystals are also often found: they crystallize in the monoclinic system, and twins are common. A granular, crystalline pure variety of gypsum, highly valued as an ornamental stone, is known as *alabaster*. Finally gypsum is often found as fibrous masses: *fibrous gypsum*; or in transparent plates, which very easily split into thin leaves, as *selenite*. Selenite is largely used for optical purposes. Gypsum may be readily prepared artificially by mixing a solution of calcium chloride with sulphuric acid or a sulphate, when it falls as a crystalline precipitate.

Crystalline gypsum is so soft that it can be scratched with the nail. As mentioned above, it is only slightly soluble in water, either hot or cold—one part requires nearly 400 parts of water for solution. The solubility is increased by the addition of common salt, so that one part of gypsum dissolves in about 120 parts of a saturated solution of common salt.

The two molecules of water which gypsum contains are only loosely united to it. It parts with the greater portion when heated up to 120°, but the residue is only expelled above 200°. Gypsum which has been heated to a temperature not much above 120° (*Plaster of Paris*) acquires the property of again uniting with water when mixed with it, and of setting to a hard mass. Plaster of Paris, prepared as above, and ground to a fine powder, is largely used for various technical purposes. When mixed with water it

soon sets hard, and can therefore be employed as a cement, which will not, however, withstand the action of water. As the hardening (with an evolution of heat) sets in soon after the plaster is mixed with water, only a small quantity must be prepared at a time; but if a strong solution of common alum is used instead of water the setting takes place more slowly, and so allows more time for manipulation. If a stronger cement is required, the plaster of Paris is first mixed with iron filings and then with water. Such a mixture is sometimes used to cement the iron parts of a building into the walls.

It is a well-known, but remarkable fact, that if gypsum is heated considerably above 120° it loses the property of uniting rapidly with water. And in the same manner, the naturally occurring anhydrous calcium sulphate (anhydrite) cannot unite with water to form a hard mass. Both forms combine, however, slowly with water when left in contact with it for a long time, and finally produce ordinary gypsum.

As the mixture of plaster of Paris and water readily adapts itself to any surface with which it is brought into contact, it is used for producing copies of coins and medals, as well as of busts and statuettes (plaster casts). It was also previously used in the process of stereotyping, in which a cast is taken of the type, and from this a second cast with fusible metal, which can then be used for printing just as the original type. Plaster casts for this purpose have now been to a large extent superseded by paper pulp, which has the special advantage that it is not so brittle as the dry plaster. If plaster of Paris is mixed with a solution of glue or gelatine instead of with water, it solidifies more slowly, and is hard enough to take a good polish. The mixture may be coloured with various metallic oxides, and is used to prepare artificial marbles, &c.

Large quantities of plaster of Paris are used to coat the interior walls and ceilings of our rooms, and it is also employed in medicine and agriculture. The surgeon uses it for the preparation of plaster bandages, which preserve a joint surrounded with them from movement; and the agriculturist employs it to impart ammonia from the air to plants sprinkled with it. Plaster of Paris has the power of absorbing ammonia, and attracts this substance when exposed to the air, yielding it again slowly to the plants with which it is in contact. Naturally occurring gypsum and anhydrite do not possess this property.

Calcium Nitrate: $\left.\begin{matrix} NO_2 \\ NO_2 \end{matrix}\right\} O_2Ca + 4H_2O$, may be easily obtained by neutralizing nitric acid with calcium carbonate, and crystallizes from its aqueous solution when evaporated down to a syrup. It is easily soluble both in water and alcohol. The salt, when freed from its water of crystallization by heating, forms a porous white deliquescent mass. Calcium nitrate is produced when lime—*e.g* that contained in the mortar of walls—is exposed to the vapours of ammonia, which, in the presence of the strong base, is then oxidized to nitric acid by the oxygen of the air.

In buildings where considerable quantities of ammonia are produced—*e.g.* in stables and cow-stalls—the quantity of calcium nitrate accumulating in the walls may often be sufficient to crystallize out in dry weather, and its deliquescent nature is one reason why the walls of such buildings are usually moist. Even the human body emits small quantities of ammonia, which is also absorbed in the walls and converted into calcium nitrate. For this reason the rubbish of old walls when extracted with water often yields considerable quantities of calcium nitrate.

Calcium Phosphate: $Ca_3P_2O_8$, or $\left.\begin{matrix} PO \\ PO \end{matrix}\right\} O_6Ca_3$. This salt is widely distributed in nature, and is sometimes found in considerable quantities; and since its immense importance in agriculture has been recognized, new localities of its occurrence have been and probably will be discovered.

To the minerals which consist essentially of calcium phosphate belong *phosphorite*, found in compact masses in some parts of Spain, Germany, and other places, and *sombrerite*, imported in large quantities from some of the islands of the Antilles, particularly Sombrero. In combination with calcium fluoride and chloride, it forms the mineral *apatite*: $3(PO)_2O_6Ca_3 + Ca(F,Cl)_2$, which is found either crystalline or in a massive form. Finally calcium phosphate is the chief mineral constituent of bones, which when burnt leave a residue of calcium phosphate and carbonate, *bone-ash*. The excrements of many animals, especially of those which are carnivorous—*coprolites* (petrified droppings), urine, guano, &c. —are all more or less rich in calcium phosphate, and are therefore valuable manures.

The calcium phosphate which we require for the growth of our

bodies, principally for the formation of bone, we derive directly and indirectly from plants, and these again, to whom it is just as necessary, absorb it by their roots from the soil. Calcium phosphate is as necessary as carbonic acid for the growth of most plants, particularly cereals. A grain of wheat, barley, or rye, planted in a soil absolutely free from phosphates, will, it is true, germinate and grow to a certain stage, but will produce no fruit. And if we sow cereals year after year on the same plot of ground, and so gradually make it poorer and poorer in calcium phosphate without returning any to the soil, the crops become less and less, and finally the ground is unfruitful.

For centuries it has been known to the farmer that he can preserve the fertility of his land by the addition of animal excrements, without suspecting what was the action of these substances. But Liebig, the founder of scientific agriculture, showed that this manure again gives to the land the mineral constituents (amongst other things) which have been abstracted from it by the harvest, and that the productiveness of the soil can be still further increased by the addition of those mineral substances which the plants require for vigorous growth.

The scientific agriculturist is, therefore, no longer satisfied with farmyard manure (which is indeed often insufficient in quantity), but adds to his land artificial manures, prepared in chemical factories from suitable materials. To these substances belongs calcium phosphate, and this compound, in the form of bone-meal, or of minerals containing it, has been successfully added to soils originally poor in calcium phosphate or from which this substance has been gradually abstracted by continuous harvests. Calcium phosphate is, however, insoluble in water, and is only slowly dissolved by water containing carbonic acid, hence it can be only slowly absorbed by the roots of the plants. A soluble calcium phosphate acts more quickly; and the farmer requires the phosphate in this form if he is to materially increase the fertility of his land. The chemical process by which this change is effected is a very simple one. Phosphorite, bone-ash, or some other mineral containing calcium phosphate is powdered and treated with about a half or two-thirds of its weight of sulphuric acid. A portion of the calcium is then converted into calcium sulphate, setting free some phosphoric acid which forms a soluble acid salt with the undecomposed calcium phosphate:—

$$\left.\begin{matrix}PO\\PO\end{matrix}\right\}O_6Ca_3 + 2SO_2(OH)_2 = 2SO_2\cdot O_2Ca + \left.\begin{matrix}PO\\PO\end{matrix}\right\}\begin{matrix}(OH)_4\\O_2Ca\end{matrix}$$

The mixture of calcium sulphate and acid calcium phosphate is not separated, but is brought in this form as a manure into trade, and is called *superphosphate.* The acid calcium phosphate is soluble in water, and when mixed with the soil is at once absorbed by the roots of the plants.

Chemically pure normal calcium phosphate can be obtained by mixing a solution of calcium chloride with one of normal sodium phosphate, or with the common acid phosphate if a little ammonia is afterwards added. The gelatinous precipitate dries to a white earthy powder. It is insoluble in water, but soluble in hydrochloric acid, from which solution it is again precipitated unchanged by ammonia.

Monacid Calcium Phosphate: $HCaPO_4$, or $PO\left\{\begin{matrix}O_2Ca\\OH\end{matrix}\right.$ is precipitated as a gelatinous mass, often becoming crystalline on standing, when a solution of calcium chloride is mixed with one of monacid sodium phosphate and acetic acid :—

$$PO\left\{\begin{matrix}(ONa)_2\\OH\end{matrix}\right. + CaCl_2 = PO\left\{\begin{matrix}O_2Ca\\OH\end{matrix}\right. + 2NaCl.$$

Like the normal salt, it is insoluble in water.

Diacid Calcium Phosphate: $H_4CaP_2O_8$, or $\left.\begin{matrix}PO\\PO\end{matrix}\right\}\begin{matrix}(OH)_4\\O_2Ca\end{matrix}$ may be obtained from the normal or monacid salt by the addition of phosphoric or hydrochloric acid, and evaporating down. It then crystallizes out in colourless tablets, which, with a small quantity of water, give a crystalline precipitate of the monacid phosphate, but which dissolve in a larger quantity of the solvent. It is the chief constituent of the manure called *superphosphate of lime*, or simply *superphosphate.*

Calcium Carbonate: $CO\cdot O_2Ca$.—This compound is very widely distributed on the surface of the earth, and in very different forms. It is prepared artificially by precipitating a solution of a calcium salt with sodium carbonate, and then forms a white amorphous powder, which soon becomes crystalline. It is insoluble in pure water, even when hot, but dissolves in water containing carbonic acid with the formation of an acid carbonate.

Calcium carbonate easily dissolves in dilute hydrochloric, nitric, or acetic acid, with evolution of carbonic acid; and when heated to redness loses its carbonic acid, and is transformed into calcium oxide.

Calcium carbonate is dimorphous: as *calcite* it crystallizes in the hexagonal system, usually in rhombohedra, while as *arragonite* it belongs to the rhombic system. Both forms may be produced artificially. If calcium carbonate is precipitated from a solution at the ordinary temperature, the precipitate is at first amorphous, but soon becomes crystalline, and then consists of minute rhombohedra like calcite; the same crystals are also formed when the clear solution of calcium carbonate in carbonic acid is allowed to evaporate slowly. But if the calcium carbonate is precipitated from a boiling-hot solution instead of from a cold one, the crystalline precipitate then consists of small rhombic prisms, resembling those of arragonite. The calcium carbonate deposited from hot springs (*e.g.* Carlsbad) usually has this form.

The numerous forms in which calcium carbonate occurs in nature are designated by different mineralogical names.

Calcite or *calc-spar* is nearly pure calcium carbonate crystallized in rhombohedra or in some other hemihedral form belonging to the hexagonal system. A variety of calcite, which is distinguished by its purity and transparency, and which is largely used in optical instruments to produce double refraction, is called *Iceland-spar.*

Arragonite is the second form in which calcium carbonate crystallizes. It is usually found in rhombic prisms, and is considerably rarer than calcite.

Marble is a granular, crystalline, compact form, produced from limestone by the action of underground heat and pressure. White marble often looks like loaf-sugar, and consists of small crystals of calcite. Marble is found in various colours from white to black.

Compact limestone, of various colours according to the impurities which it contains, forms large mountain masses. It has nearly all been produced by the agency of marine animals, whose remains are often found petrified in it. *Oolitic limestone, freestone*, consists of numerous small globular masses of calcium carbonate cemented together, and is so called because it resembles the roe of a fish. *Lithographic stone* is a compact, fine-grained form of limestone, found near Solenhofen, in Bavaria, and largely used in the processes of lithography.

Chalk is a soft, earthy variety of calcium carbonate, and from its white colour is apparently very pure. It consists chiefly of the minute cases of various species of foraminifera, and has been formed in deep seas. That it still contains organic traces of these animals is readily proved by dissolving it in dilute hydrochloric acid. The carbonic acid evolved possesses an unpleasant odour, and a brown organic residue remains behind.

Calcareous tufa or *travertine* is a porous form of calcium carbonate, produced by the gradual evaporation of a carbonic acid solution of the carbonate. Of a similar origin are the *stalagtites* found hanging from the roofs of limestone caves, and other similar deposits.

Finally, calcium carbonate is a constituent of many products of animal life—*e.g.* of egg-shells, and of the shells of oysters, and other mollusca. On some parts of the coast, where lime is scarce, oyster-shells are burnt to obtain quick-lime.

The technical applications of calcium carbonate are exceedingly numerous and important. Marble is a valuable material for the builder and sculptor. Chalk is used for writing, and, when finely powdered, as a pigment. Compact limestones are employed for the manufacture of glass, and as a flux to produce a fusible slag in the extraction of many metals from their ores. And, finally, immense quantities of limestone are used for the manufacture of quick-lime and then of mortar.

Bleaching Powder. (*Chloride of Lime.*)—The chief compound contained in this important substance has (p. 117) the composition: $Ca(OCl)Cl$ or $Ca\begin{cases}OCl\\Cl\end{cases}$ but the pure compound corresponding to this composition has not yet been prepared. Bleaching powder is a soft, white, amorphous powder, with a faint odour of hypochlorous acid, soluble in water with decomposition into calcium chloride and calcium hypochlorite and easily decomposed by all acids.

Bleaching powder is manufactured on a large scale by saturating dry slaked-lime with chlorine. The gas is generated in leaden retorts and led into chambers containing shelves on which the slaked-lime is placed in thin layers. As soon as the lime ceases to absorb the gas, the process is finished; the chambers are then opened and the bleaching powder preserved in well-closed vessels.

A solution of bleaching powder in water does not itself bleach, or only very slowly as it is decomposed by the carbonic acid of the air. If, however, a dilute acid is added, the bleaching-powder is decomposed, yielding hypochlorous acid, and then free chlorine. The articles to be bleached are first thoroughly cleansed, dipped into a dilute solution of bleaching powder, and then into a very dilute solution of hydrochloric acid, which, with the bleaching powder they contain, liberates free chlorine (p. 117). Thorough washing is necessary afterwards, as any small traces of chlorine which remain behind gradually rot the stuff. But as it is impossible to completely remove the last traces of chlorine, it is customary to dip the articles in a solution of some substance which acts chemically upon it—called an antichlor. Such a substance is sodium thiosulphate (p. 370).

The formula given above for bleaching powder and the assumption that it is decomposed by water are supported by many facts. The action of this substance on bodies which easily take up chlorine and oxygen is quite different in the absence and in the presence of water. Absolute alcohol and dry bleaching powder react energetically upon one another and produce first ethyl hypochlorite, and then acetic ether, but if aqueous alcohol is used, the chief product is chloroform.

We have already seen (p. 117) that a solution of bleaching powder yields calcium chloride and chlorate when boiled.

Calcium Silicate: $SiO \cdot O_2Ca$.—The normal salt of this composition is produced as a gelatinous precipitate, drying to a white amorphous powder, when calcium chloride in solution is added to a solution of sodium silicate. This compound is found in nature as the mineral *wollastonite*, and united with other silicates as double salts. To these belong many of the *zeolites*, *lime-garnet*, *datolite*, &c. Similar double silicates, but not crystalline, are the chief varieties of

GLASS.

This important substance is essentially a double silicate of potash or soda and lime, in which the lime is sometimes displaced by lead oxide. It is distinguished by its transparency, hardness, fusibility and resistance to many solvents which attack other substances, even the metals, and is therefore indispensable to the chemist.

Glass is manufactured by fusing together a mixture of calcium carbonate, potassium (or sodium) carbonate and silica at a high temperature, in specially constructed furnaces and crucibles. At a bright-red heat the silica expels the carbonic acid from the carbonates, producing a double silicate of calcium and potassium or sodium, which on continued heating forms a homogeneous liquid, and on cooling solidifies to a transparent glass without a trace of crystalline structure. The purer the materials employed, the purer and less coloured is the glass obtained. In order to give the required shape to the glass it is partly cast and partly blown. Large slabs of thick glass (plate-glass) are obtained by pouring the liquid substance on to horizontal slabs of iron, and the commoner kinds of glass vessels (bottles, tumblers, &c.), especially the thicker ones, are cast in moulds, just as liquid iron is cast. The majority of glass vessels are, however, made of what is called blown glass. The workman takes a mass of semi-fluid glass on the end of an iron tube, and by blowing, combined with various movements which cannot be well described, gives to it almost any desired shape. Most of the various shaped vessels used in daily life, and in the laboratory—wine-glasses, bottles, funnels, flasks, &c.—are made in this way.

Glass is a brittle substance, and if of considerable thickness, or rapidly cooled, easily breaks when subjected to rapid changes in temperature. In order to allow the molecules of the glass to arrange themselves regularly, that the tension on cooling may be the same throughout the entire thickness, it must be *annealed*, or allowed to cool slowly. For this purpose, the glass vessels, after they have been made, are brought into the annealing furnaces, where the glass is heated nearly to the temperature at which it becomes soft, and then allowed to cool very slowly during several days or even weeks. The influence which rapid cooling has on the properties of the glass is well seen in what are called Rupert's drops, which are made by dropping liquid glass into cold water. Owing to the rapid cooling, they are hard, and stand pressure or even a blow. But if slightly scratched, or if a small piece is broken off the thin end, the whole drop breaks up into small pieces of glass.

A few years ago a variety of quickly annealed glass was introduced into trade, and highly recommended for various purposes. This *toughened glass*, as it is called, is harder than common glass, and bears rapid changes of temperature better. It is prepared by dipping the freshly blown hot glass into a bath of hot oil or paraffin,

a process which resembles that by which Rupert's drops are formed, except that the cooling is less sudden. Vessels prepared in this way may be dropped from a considerable height on to the floor without breaking, and a glass dish filled with cold water may be placed on glowing charcoal, but, like Rupert's drops, they will not stand the slightest scratch. A sharp grain of sand is often sufficient to cause their violent fracture into a number of small pieces, and it sometimes happens that vessels of toughened glass, which have been used for years, and have withstood considerable changes of temperature without damage, suddenly break up into a thousand pieces. Toughened glass vessels, from which so much was expected at the time of their introduction, should therefore never be used, especially for chemical apparatus.

Various kinds of glass are distinguished from one another according to their constituents, and according to the purity of the substances employed in their manufacture. *Potash*, or *hard-glass* is a double silicate of calcium and potassium, and is largely manufactured in Bohemia. It is less acted on by chemical reagents than any other kind of glass, and when the proportion of silica is high, is difficultly fusible. The glass tubes used for combustions in organic analysis are made from this difficultly fusible glass. *Crown*, or *soda-glass*, contains soda instead of potash, and is the common window-glass. It is more easily fusible than potash-glass, and more readily attacked by acids. *Bottle-glass* is a coarse form of crown-glass, made with impure materials, and more or less coloured by the presence of iron. It also contains not inconsiderable quantities of aluminium silicate. *Flint-glass* is a double silicate of lead and potassium—*i.e.* it is potash-glass in which the calcium has been displaced by lead. It is prepared by fusing together silica, potassium carbonate, and lead oxide (litharge), and is distinguished by its lustre and high index of refraction. Flint-glass is the most easily fusible of all glasses, and the most easily attacked by acids; large quantities of it are manufactured in England and France. Flint-glass is especially valuable for optical purposes, owing to its high index of refraction. The refractive power of the glass can be increased by using a larger proportion of lead oxide; such glass, called *strass*, is used for the manufacture of artificial gems.

Finally, the various slags obtained in metallurgical operations are also a species of glass. In smelting some of the heavy metals, especially iron, calcium carbonate is often added as a flux to form

a fusible slag, which removes the earthy impurities, swims on the surface of the heavier metal, and so protects it from the oxygen of the air. The slags consist of the silicates of the alkalies, of lime, alumina, magnesia, iron, &c., and when cold yield a strongly coloured, often opaque, vitreous mass.

Glasses of various colours are produced by the addition of different metallic oxides to the liquid glass. The silica of the glass unites, like borax, with these oxides, forming coloured silicates. Blue glass is produced by the addition of small quantities of cobalt; green by uranium or chromium; olive-green by ferrous oxide; yellow or brown by ferric oxide; amethyst by manganous oxide; red by cuprous oxide, or a trace of gold, &c. Coloured glass often consists of colourless glass with the coloured glass on one side only. Such glass is said to be *flashed.* White, opaque, or *milk-glass*, is made by adding some white infusible powder, such as bone-ash, or cryolite, to the molten glass.

Calcium Oxalate: $\left.\begin{matrix}CO\\CO\end{matrix}\right\}O_2Ca + H_2O$, is contained in many plants, especially in the sorrels, and is obtained by precipitating a solution of calcium chloride with ammonium oxalate. The precipitate is crystalline, and loses its water of crystallization at 100°. The salt is insoluble both in water and in dilute acetic acid, and serves, therefore, for the estimation of calcium and of oxalic acid.

Calcium Chloride: $CaCl_2$.—This salt, which is distinguished by the energy with which it attracts water, and which is, therefore, largely used for drying purposes in chemistry, is obtained as a bye-product in many operations—*e.g.* in the preparation of ammonia from ammonium chloride and quick-lime (p. 184), and of carbonic acid from calcium carbonate and hydrochloric acid. The acid liquid resulting from the latter process when evaporated down to a small bulk deposits large rhombic crystals of the composition: $CaCl_2 + 6H_2O$. These crystals deliquesce in the air and dissolve readily in water with a considerable fall in temperature; and when mixed with snow or powdered ice the temperature may fall as low as $-45°$. If this crystalline compound is heated, it melts in its water of crystallization and loses 4 molecules of water, leaving a white porous mass, which readily absorbs water again. At a red heat the salt loses all its water and fuses to a clear liquid. This fused mass is poured on to a clean iron plate, broken into

pieces when cold, and so brought into trade. Fused calcium chloride dissolves in water with evolution of heat; it is also soluble in alcohol. It energetically absorbs dry ammonia gas, producing a compound: $CaCl_2 + 8NH_3$, which is decomposed into its components either when heated or when brought into contact with water. Calcium chloride cannot, therefore, be used to dry gaseous ammonia.

Calcium Fluoride: CaF_2, is the mineral *fluor-spar*. It crystallizes in the regular system, but is also found in compact masses. When finely powdered it is used for the preparation of hydrofluoric acid, and as a flux to produce a fusible slag—hence its name (from *fluo*, I flow). Calcium fluoride is quite insoluble in water, and is therefore precipitated when a solution of a calcium salt is mixed with one of a soluble fluoride.

Calcium Sulphide: CaS, is obtained as a yellowish-white earthy mass by glowing quick-lime in a stream of sulphuretted hydrogen, or, less pure, by igniting a mixture of powdered calcium sulphate and charcoal, when calcium sulphide and carbonic oxide are formed. The compound so produced is insoluble in water, but gradually decomposes in contact with this liquid into calcium hydrate and sulphydrate:—

$$2CaS + 2H_2O = Ca(OH)_2 + Ca(SH)_2.$$

Calcium sulphide, like the other sulphides of the alkaline earths, shines in the dark after it has been exposed to a bright light—in other words, it phosphoresces. It is the chief constituent of *Balmain's luminous paint*, in which form it is used to render match-boxes, buoys, and other objects luminous in the dark.

Calcium Sulphydrate: $Ca(SH)_2$, is easily obtained in solution by saturating milk of lime with sulphuretted hydrogen. It possesses the property of softening hair and changing it into a gelatinous mass. Mixed with other substances, it is used by some Oriental nations as a depilatory.

Calcium Pentasulphide: CaS_5.—A mixture of this salt and calcium thiosulphate may be prepared by boiling milk of lime with an excess of flowers of sulphur, and filtering off the reddish-coloured liquid. Like potassium pentasulphide, hydrochloric acid decomposes it with a copious precipitate of milk of sulphur (p. 145).

Detection of Calcium Compounds.

Calcium compounds when introduced into a non-luminous gas-flame give a reddish colour, somewhat yellower than that produced by the compounds of strontium. The spectra of the two flames are, however, so different, that they may be very easily distinguished from one another. If the compound is an insoluble one, it must be first moistened with hydrochloric acid before it is introduced into the flame.

Calcium salts closely resemble those of strontium and barium. The sulphates are all difficultly soluble in water, that of calcium being the most soluble. The carbonates are all equally insoluble in water, whence it follows that they are all precipitated together by sodium or ammonium carbonate. The oxalates are also all insoluble in water, but that of calcium is distinguished from the other two by its insolubility in acetic acid. Of the anhydrous nitrates only that of calcium is soluble in absolute alcohol, a fact which is utilized to separate calcium from strontium and barium.

STRONTIUM.

Chemical Symbol: Sr.—*Atomic Weight*: 87·5.

The compounds of this element closely resemble those of calcium and barium, especially the latter, and strontium with its compounds forms a natural transition from calcium to barium.

The most important minerals containing strontium are *celestine* or strontium sulphate, and *strontianite*, strontium carbonate. The latter mineral is called from Strontian in Scotland, where it was first found in quantity, hence the name given to the element.

Recently, large deposits of strontianite have been found in Westphalia, and this mineral is now almost exclusively used for the preparation of strontium compounds.

The metal may be obtained by the electrolysis of the fused chloride. Its specific gravity is 2·5, it is harder than lead, and is malleable. Strontium, like calcium, is a yellow metal and melts at a red heat.

Strontium Oxide: SrO, cannot be prepared, like calcium oxide, by glowing the carbonate, as this compound is only slowly

and incompletely decomposed by heat. It is obtained, like barium oxide, by heating its nitrate to redness, and forms a grey, porous mass.

This oxide unites with water and produces the hydrate: $Sr(OH)_2$, which crystallizes from water as the compound $Sr(OH)_2 + 8H_2O$. Strontium hydrate is more soluble in water than the calcium compound, but less than that of barium; 1 part dissolves in about 60 parts of cold water. The solution is strongly alkaline.

Strontium Peroxide: SrO_2 is obtained, like the calcium compound, by precipitating a solution of strontium hydrate with hydrogen peroxide. Strontium oxide does not unite directly with oxygen.

Strontium Sulphate: $SO_2 \cdot O_2Sr$, is found in nature, as the mineral *celestine*, in transparent, rhombic prisms, often of considerable beauty. The salt may be obtained as a white powder by precipitating a solution of a strontium salt with sulphuric acid or a soluble sulphate. It is slightly soluble in water, but less so than calcium sulphate; 1 part of the salt requires about 6,000 parts of water for solution.

Strontium Nitrate: $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\} O_2Sr$, is distinguished from calcium nitrate by its insolubility in alcohol, and in other respects resembles the barium salt. It is easily obtained by dissolving strontianite in dilute nitric acid and evaporating down. As strontium compounds impart a red colour to flames into which they are introduced, its nitrate is used instead of potassium nitrate to produce an inflammable powder which burns with a red light.

Strontium Carbonate: $CO \cdot O_2Sr$, is obtained artificially like the calcium compound, which it closely resembles. It occurs in nature as the mineral *strontianite*, either in rhombic prisms or in indistinct crystalline masses.

Strontium Chloride: $SrCl_2 + 6H_2O$, crystallizes in needles, is easily soluble in water and slightly deliquesces in the air. Like calcium chloride, it is soluble in strong alcohol.

Strontium Sulphide: SrS, is obtained from celestine by heating a mixture of the powdered mineral with charcoal, and forms the starting-point in the preparation of strontium compounds from this source. Like calcium sulphide, it is luminous in the dark.

Detection of Strontium Compounds.

Strontium compounds impart an intense crimson colour to the non-luminous flame, which can at once be distinguished from the lithium or calcium flame by the spectroscope. The spectrum of strontium is especially characterized by a fine line in the bright blue.

Strontium salts are distinguished from those of calcium by the fact that calcium sulphate produces a precipitate of strontium sulphate on standing, or warming; they give no precipitate with potassium chromate, especially if the solution contains free acetic acid, although the chromate is less soluble than the calcium salt.

Strontium nitrate is insoluble in strong alcohol, and thus differs from calcium nitrate. This property affords a ready means of quantitatively separating the two salts.

BARIUM.

Chemical Symbol: Ba.—*Atomic Weight*: 137.

This element, which derives its name from the high specific gravity of its compounds (βαρύς = heavy), is found in nature like strontium chiefly as the sulphate, *barite* or *heavy spar*, and as the carbonate, *witherite*. The former compound is the source from which nearly all barium compounds are prepared.

Metallic barium is exceedingly difficult to prepare. It is said to have been obtained by electrolysis of the fused chloride, and is described as a yellow metal, melting at a bright red heat and decomposing water at the ordinary temperature.

Barium, like calcium and strontium, is a diad element in nearly all its compounds; in the peroxide: BaO_2, it is possibly a tetrad.

Barium Oxide (*Baryta*): BaO, cannot be prepared by heating the carbonate, as the carbonic acid is more firmly united even than in strontium carbonate, and is only very slightly expelled even at the highest temperatures. Barium oxide is best prepared by heating barium nitrate. A Hessian crucible is about half filled with the salt and heated first gently to expel most of the nitric peroxide, and then, when the frothing has subsided, to bright redness. The oxide which remains behind is a grey porous mass, which has

apparently been fused, but is really infusible at this temperature. Occasionally it has a greenish colour, due to manganese derived from the crucible which has been converted into barium manganate. When mixed with water, it evolves a considerable amount of heat and is converted into barium hydrate. When gently heated in the air or oxygen, it absorbs considerable quantities of oxygen and is changed into barium peroxide.

Barium Hydrate: $Ba(OH)_2$.—The preparation of barium hydrate from barium oxide is tedious and unsuitable if large quantities are required. It is better to employ the sulphide, which is easily obtained from the sulphate by heating with powdered charcoal. For this purpose a solution of the sulphide in water is boiled with copper oxide until a portion of the liquid no longer blackens a solution of lead acetate. The clear solution is then filtered off from the insoluble copper sulphide. The reaction is expressed in the following equation :—

$$BaS + CuO + H_2O = Ba(OH)_2 + CuS.$$

From the hot solution so obtained, crystals of the compound: $Ba(OH)_2 + 8H_2O$ separate out on cooling in tablets or prisms. Barium hydrate may also be prepared from the sulphide by first converting this salt into the carbonate by moist carbonic acid—sulphuretted hydrogen being set free—and then acting on the carbonate with superheated steam—*i.e.* steam at high pressure. The carbonic acid then passes away with the steam, and barium hydrate remains behind. The crystalline compound parts with its water of crystallization when heated, but, unlike calcium hydrate, cannot be converted into the oxide by heat.

Barium hydrate dissolves in about 20 parts of cold water, but requires less than 1 part of hot water for solution. It is thus much more easily soluble than calcium or strontium hydrate. The solution (*baryta-water*) is strongly alkaline and precipitates the weaker bases from their solutions like caustic potash. When exposed to the carbonic acid of the air it becomes turbid more rapidly than lime-water. Baryta is a weaker base than potash or soda, and is therefore precipitated by these alkalies, not by ammonia, from concentrated solutions of its salts.

Barium oxide possesses the remarkable property of forming an insoluble compound with cane-sugar ; and on this account large quantities are used by sugar refiners. Strontium oxide also possesses this property.

Barium Peroxide: BaO_2.—Barium oxide, when heated to *faint* redness in a stream of air or oxygen, increases in weight owing to absorption of oxygen, and becomes gradually converted into barium peroxide, which cannot be distinguished by its external properties from the oxide itself. At a slightly higher temperature than that required for its production, but still far below bright redness, it again parts with an atom of oxygen, and is reconverted into the oxide, which can again unite with oxygen, and so on. By utilizing these reactions, large quantities of pure oxvgen may be obtained from the air. It is important that the air used for this purpose should be freed, by passing it over lime, from carbon dioxide. Otherwise barium carbonate, a very stable substance, is formed, and thus the baryta gradually loses its power of absorbing oxygen. Later it was discovered that barium peroxide parts with *its oxygen at the same temperature at which it is produced if the pressure is reduced. Or, in other words, to obtain a supply of pure oxygen, the barium oxide is kept at a constant temperature, and the pressure only varied.* Possibly some use may be made of this interesting fact.

Barium peroxide prepared as above described is never pure, but always contains more or less barium oxide. It may be purified in the following way. It has already been stated (p. 90) that barium peroxide is distinguished from manganese and other peroxides by the fact that it gives hydrogen peroxide, not chlorine, when treated with hydrochloric acid, and its purification depends upon this reaction. The impure barium peroxide, obtained by heating barium oxide in a stream of air, is finely powdered and rubbed up with water in a mortar, with which it unites chemically. The mixture is next gradually added to dilute hydrochloric acid, until the liquid only reacts faintly acid, and the clear solution, containing barium chloride and hydrogen peroxide besides the excess of acid, filtered off. On adding an excess of baryta-water to this liquid, the pure hydrated peroxide separates out in lustrous tablets of the composition: $BaO_2 + 8H_2O$. These crystals when washed, and dried between filter paper and over sulphuric acid, gradually lose all their water and leave pure barium peroxide behind. The pure compound remains unchanged in the air, gives up one-half of its oxygen when heated, and unites with water to form the hydrated compound.

Barium Sulphate: $SO_2 \cdot O_2Ba$.—This salt, the most important naturally occurring compound of barium, is usually found

in compact masses, and sometimes in tabular crystals belonging to the rhombic system. It has a specific gravity of 4·4, and is known as *barite* or *heavy-spar*. It may be readily prepared artificially, as a heavy, white precipitate, by adding sulphuric acid or a sulphate to a soluble barium salt. Barium sulphate is quite insoluble both in water and dilute acids, and is therefore used to precipitate barium or sulphuric acid from a liquid. Concentrated sulphuric acid dissolves it to some extent, but on dilution with water it is again precipitated, like lead sulphate. Precipitated barium sulphate is used as a white pigment under the name of *permanent white*; it is also largely used to adulterate white-lead and to weight paper, for which purposes its high specific gravity, combined with its cheapness, makes it admirably adapted.

Barium Nitrate: $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\} O_2Ba$, is prepared by dissolving witherite or barium sulphide in nitric acid, and is deposited from the hot solution in brilliant, heavy octahedra, without water of crystallization. The salt is tolerably easily soluble in water, especially when hot, but less soluble in the presence of free acid; hence, on adding nitric acid to an aqueous solution, a precipitate is produced. It is insoluble in alcohol. Barium nitrate is poisonous, like nearly all the barium salts.

Barium Carbonate: $CO \cdot O_2Ba$, occurs in nature as the mineral *witherite*, and is thrown down as a white precipitate on adding sodium carbonate to a solution of a barium salt. It is insoluble in water, but slightly soluble in the presence of carbonic acid; and, notwithstanding its insolubility, is poisonous.

Barium Chloride: $BaCl_2 + 2H_2O$.—This compound is one of the least soluble of the barium salts. It is prepared in a similar manner to the nitrate, and crystallizes in rhombic plates. At 100° it loses its water of crystallization and melts at a red heat. Alcohol does not dissolve it—a reaction which is employed to separate barium from calcium and strontium. Its aqueous solution is largely used in analytical chemistry as a test for various acids.

Barium Sulphide: BaS; and *Barium Sulphydrate*: $Ba(SH)_2$. Barium sulphide is obtained as a white amorphous mass when

barium oxide is heated in a stream of sulphuretted hydrogen, or, less pure, by reducing the sulphate with charcoal. An intimate mixture of finely powdered heavy-spar and charcoal is mixed with starch paste and formed into balls. These are then dried in the air, placed between alternate layers of charcoal in a furnace, the bottom layer of which is ignited. When cold, they are extracted and digested with water. The solution, especially if prepared hot, does not contain barium sulphide, but a mixture of barium sulphydrate and hydrate, which crystallize together :—

$$2BaS + 2H_2O = Ba(SH)_2 + Ba(OH)_2.$$

If sulphuretted hydrogen is led into this solution, the hydrate is converted into sulphydrate, and this salt alone crystallizes out on evaporation. As heavy-spar is a much commoner mineral than witherite, barium sulphide is the compound from which nearly all other barium salts are manufactured.

Detection of Barium Compounds.

Compounds of barium when introduced into a Bunsen flame produce a yellowish-green colour, the spectrum of which is more complicated than that of either calcium or strontium, and is distinguished by *several* lines in the green.

In their chemical characters the barium compounds closely resemble those of calcium and strontium, but it is still easy to distinguish them from one another. Barium sulphate is so insoluble in water, that on adding a solution of calcium sulphate to one of a barium salt an *immediate* turbidity is produced. In the same manner calcium and strontium chromates are much more soluble than barium chromate, and potassium chromate added to a dilute solution of barium chloride produces a pale yellow precipitate of barium chromate, but no precipitate is produced with calcium (or strontium) chloride. Barium can be separated from calcium or strontium by digesting the perfectly dry chlorides with absolute alcohol. Calcium and strontium chlorides then dissolve while barium chloride remains undissolved.

MAGNESIUM.

Chemical Symbol: Mg.—*Atomic Weight*: 24.

The compounds of magnesium are not less widely distributed than those of calcium, but are not found in such large quantities. Among the more important minerals containing magnesium are: *magnesite* (magnesium carbonate: $CO \cdot O_2Mg$), *dolomite* (magnesium-calcium carbonate: $CO \cdot O_2Mg + CO \cdot O_2Ca$), *talc*, *steatite* or *soap-stone*, *serpentine*, and *meerschaum* (all essentially magnesium silicate). Other silicates which are rich in magnesium are: *augite*, *hornblende*, *asbestos*, *olivine*, and *biotite* or *magnesium mica*. Magnesium also occurs in combination with sulphuric acid as Epsom salt in many mineral waters and in the sea.

Magnesium is a malleable silver-white metal of specific gravity = 1·75. It melts at 700° to 800°, and at about 1000° can be distilled. It remains almost unchanged when exposed to the air, and only becomes covered with a thin, grey coating of the oxide which preserves the metal from further oxidation. When heated in the air above its melting-point it catches fire and burns with a brilliant white light, producing its only oxide—magnesia. A wire or thin ribbon of magnesium very easily takes fire and burns when one end is held in the flame of a Bunsen burner. The light of burning magnesium is so intense and so rich in chemical rays that a mixture of chlorine and hydrogen explodes when exposed to it, just as it does in bright sunlight.

Magnesium does not decompose water at the ordinary temperature, or at all events only very slowly; at about 30° a feeble evolution of hydrogen begins, which becomes more rapid as the temperature rises. Dilute acids, as well as ammonium chloride or carbonate, readily dissolve it.

Magnesium may be prepared either by the electrolysis of the fused chloride, or else by decomposing the chloride with sodium. The electrolysis of the chloride may be performed in a porcelain crucible partially divided into two divisions by a piece of unglazed porcelain (fig. 63). When the crucible has been filled with the fused chloride, the two electrodes, which are made of gas-carbon and fitted in the lid (fig. 64), are introduced and connected with the poles of a powerful battery (about 8 to 10 Bunsen cells). The metal which is then produced is lighter than the fused chloride, and would rise to the surface and burn in the air if the negative pole were not

provided with a series of notches which catch the globules of metal in their ascent.

For the reduction of magnesium from the chloride by sodium, a mixture is prepared of six parts of anhydrous magnesium chloride,

Fig. 63.

Fig. 64.

one part of fluor-spar, one part of fused potassium-sodium chloride, and one part of sodium cut into small pieces, and the whole thrown into a red-hot Hessian crucible. As soon as the first violent reaction is over, the closed crucible is removed from the furnace, and when it is no longer red hot, its contents are stirred with a piece of tobacco-pipe to unite the smaller globules of metal into larger ones. When the crucible is cold it is broken open, and the globules of metal picked out and washed with water.[1]

Magnesium is a diad in all its compounds; it unites in only one proportion with oxygen.

Magnesium Oxide. *Magnesia*: MgO.

This, the only oxide of magnesium, is a white, light powder, which is infusible at the highest temperatures of our furnaces. When strongly heated it becomes much denser, and its specific gravity increases from 3·2 to 3·6. It is especially distinguished from the oxides of calcium, strontium, and barium by its almost complete insolubility in water. But although one part of magnesia requires more than 50,000 parts of water for solution, it still produces a distinctly blue spot when moistened with water and placed on red litmus paper. It unites with water with a very slight evolution of heat, forming the hydrate, from which the water is again easily expelled on heating. It attracts carbonic acid from the air (when in the pulverulent state), and, being a strong base, forms compounds with all acids.

[1] See Appendix.

Magnesium oxide is obtained by gently glowing the basic carbonate, known to pharmacists as *magnesia alba*, and then gives a fine white powder called *magnesia usta* or *calcined magnesia.* The oxide is produced as a solid, hard mass on glowing magnesite, the compact natural form of magnesium carbonate. Magnesium oxide gradually hardens in contact with water, and forms a compact mass of the hydrate.

Magnesium Hydrate: $Mg(OH)_2$, is precipitated on adding caustic soda or ammonia to a solution of magnesium sulphate; when washed and dried, it yields a white powder. It may be heated to 100° without losing its water of hydration, and slowly attracts carbonic acid from the air. It is found in nature as the mineral *brucite.*

Magnesium Sulphate. *Epsom Salt*: $SO_2 \cdot O_2Mg + 7H_2O$.—This salt differs from the sulphates of calcium, strontium, and barium, by its easy solubility in water, and by the readiness with which it crystallizes. Considerable quantities of magnesium sulphate united with one molecule of water are found in the Stassfurt beds, and are known as *Kieserite*: $SO_2 \cdot O_2Mg + H_2O$.

Magnesium sulphate is further contained in sea-water and in many highly valued mineral waters, among which may be mentioned those of Epsom near London, Seidlitz, Friedrichshall in Germany, and Hunyadi János in Hungary. The salt may be obtained artificially by decomposing magnesite or dolomite with dilute sulphuric acid, and is a bye-product in manufactories of aërated waters when either of these substances is used to prepare carbonic acid. If dolomite is used, calcium sulphate remains undissolved.

Magnesium sulphate crystallizes in colourless rhombic prisms, and possesses an unpleasant saline and bitter taste. It is easily soluble in water, insoluble in alcohol, and when heated melts in its water of crystallization, of which it loses six molecules under 150°. The last molecule is only expelled at a temperature above 200°. This molecule of water—so-called *water of constitution*—can be displaced by salts, producing double compounds, containing six molecules of water. Thus, when solutions of magnesium and potassium sulphates are mixed, a double salt of the composition: $SO_2 \cdot O_2Mg + SO_2(OK)_2 + 6H_2O$, crystallizes out. In this respect magnesium sulphate is closely allied to other sulphates of diad

metals which also crystallize with seven molecules of water (the vitriols), and thus connects the metals of the alkaline earths with the heavy metals.

Owing to its well-known action as a mild and safe purgative, magnesium sulphate is a valuable and much used medicine, and mineral waters containing it are among those of which the largest quantities are consumed.

Magnesium Phosphates.

The *normal salt*: $(PO)_2O_6Mg_3$, is obtained as a white precipitate on mixing a solution of normal sodium phosphate with one of magnesium sulphate. If common (monacid) sodium phosphate is added to magnesium sulphate the *monacid phosphate*: $PO\begin{cases}O_2Mg\\OH\end{cases} + 7H_2O$, is produced, which separates from concentrated solutions as a white, amorphous powder, and is slowly deposited from dilute solutions in the crystalline form. The salt is difficultly soluble in water, but easily dissolves in acids and in salts of ammonium. If ammonia is added to a solution of magnesium phosphate in ammonium chloride, or to a mixture of magnesium sulphate, ammonium chloride, and sodium phosphate, a crystalline precipitate at once separates which is insoluble both in ammonium salts and in water containing free ammonia. This compound is a double phosphate of magnesium and ammonium and has the composition: $PO\begin{cases}O_2Mg\\ONH_4\end{cases} + 6H_2O$. If heated it loses its water of crystallization and ammonia, while *magnesium pyrophosphate* remains behind, according to the equation :—

$$2PO\begin{cases}O_2Mg\\ONH_4\end{cases} = O\begin{cases}PO\cdot O_2Mg\\PO\cdot O_2Mg\end{cases} + H_2O + 2NH_3.$$

The insolubility of this ammonium-magnesium phosphate renders it a suitable compound for quantitatively estimating both magnesium and phosphoric acid. The salt is often found in decomposing urine, and is sometimes deposited in the bladder as a constituent of urinary calculi. It is also contained in guano and occasionally in old dung-heaps, often forming large, well-developed crystals (*struvite*).

Ammonium-Magnesium Arsenate: $AsO\begin{cases}O_2Mg\\ONH_4\end{cases} + 6H_2O$, is

prepared like the corresponding phosphate by mixing solutions of magnesium sulphate, ammonia, and sodium arsenate. Its properties closely resemble those of the phosphate with which it is isomorphous. When heated it also leaves a residue of *magnesium pyrarsenate.*

Magnesium Carbonate : $CO \cdot O_2Mg$.—This insoluble salt is found in nature as *magnesite*, partly crystallized in rhombohedra isomorphous with calcite, and partly as compact crystalline masses. *Dolomite* is a double carbonate of calcium and magnesium carbonate. When a magnesium salt is precipitated with sodium carbonate, a basic, not the normal salt is produced. This basic carbonate, or compound of normal magnesium carbonate and magnesium hydrate, has a varying composition, but may be generally represented either as : $3CO \cdot O_2Mg + Mg(OH)_2$ or $2CO \cdot O_2Mg + Mg(OH)_2$, with varying quantities of water. Acid sodium carbonate is produced at the same time in which a small quantity of the magnesium carbonate remains dissolved. This white precipitate is brought into trade as *magnesia alba*. (See Appendix.)

Magnesium carbonate forms double salts with the carbonates of the alkalies, which may be obtained by digesting magnesia alba with the acid alkaline carbonates.

Magnesium Borate is deposited on boiling a solution of magnesium sulphate with one of borax, but dissolves again on cooling. Magnesium borate in combination with magnesium chloride forms the mineral *boracite*, crystallizing in the regular system.

Magnesium Silicate : $Si(O_2Mg)_2$.—The normal salt of this composition occurs in nature as the mineral *olivine*. The minerals *talc*, *steatite*, *serpentine*, and *meerschaum* are compounds of magnesium silicate with varying quantities of water. *Augite*, *hornblende*, and *asbestos* are double silicates of magnesium and calcium.

Magnesium Chloride : $MgCl_2$.—This salt is contained in sea-water and many mineral springs. It is obtained pure by dissolving magnesia alba in hydrochloric acid, adding chlorine water to oxidize the iron, and then digesting the solution with a slight excess of magnesia alba to precipitate the iron and alumina. The clear solution when evaporated down to a small bulk deposits very deliquescent crystals of the composition : $MgCl_2 + 6H_2O$. The water

cannot be expelled from this hydrated compound by heating, since the chloride then decomposes into magnesia and hydrochloric acid :—

$$MgCl_2 + H_2O = MgO + 2HCl,$$

and a basic chloride is formed. This decomposition can, however, be prevented by the addition of ammonium chloride, as a mixture of magnesia and ammonium chloride when heated produces magnesium chloride, ammonia and water :—

$$MgO + 2NH_4Cl = MgCl_2 + 2NH_3 + H_2O.$$

The concentrated aqueous solution is therefore mixed with enough ammonium chloride to form the double compound : $MgCl_2 + NH_4Cl$, and then thoroughly dried. The dried mass is afterwards gently heated in a Hessian crucible until vapours of ammonium chloride are no longer given off and the whole fuses quietly. The fused salt is poured on a clean slab of iron, rapidly broken into pieces and preserved in well-closed vessels. Some basic salt usually remains behind in the crucible.

Anhydrous magnesium chloride is a white crystalline mass, deliquescing in the air. It can be distilled in a stream of hydrogen at a bright-red heat, and gives a colourless, soft distillate, which solidifies to a crystalline mass of brilliant plates. The salt is easily soluble both in water and alcohol.

Magnesium chloride forms double salts not only with ammonium chloride, but also with potassium and other chlorides. Potassium-magnesium chloride : $KCl, MgCl_2, + 6H_2O$ is found in considerable quantities at Stassfurt, and is known as *carnallite*.

Detection of Magnesium Compounds.

Magnesium compounds do not colour a non-luminous gas flame when introduced into it, neither do they produce any characteristic spectrum. In this respect, magnesium differs from the other metals of the alkaline earths, and resembles those of the earths. It is further distinguished from the former by the solubility of its sulphate, and by the fact that solutions of its salts are not precipitated by ammonium carbonate, although magnesium carbonate is nearly as insoluble in water as the carbonates of calcium, strontium, and barium. The reason of this is that all insoluble magnesium compounds, except the double phosphate and arsenate of ammonium and magnesium, form soluble double compounds with ammonium salts. Hence a solution of magnesium sulphate

to which ammonium chloride has been added gives no precipitate of magnesium hydrate with ammonia.

From these reactions, magnesium salts may be just as readily detected and separated as those of the other alkaline earths. From calcium, which commonly accompanies it, it may be separated by adding ammonium chloride and ammonia to the mixed solution, and then ammonium oxalate or carbonate. All the calcium is then precipitated as calcium oxalate or carbonate, and all the magnesium is contained in the filtered solution, from which it may be thrown down with sodium phosphate as ammonium-magnesium phosphate.

It is remarkable that ammonia (in the absence of ammonium salts) partly precipitates magnesia from neutral solutions, while in solutions of calcium, strontium, and barium it produces no precipitate.

BERYLLIUM.

Chemical Symbol: Be.—*Atomic Weight*: 9·1

This somewhat rare element is chiefly found in nature as a double silicate of aluminium and beryllium: $3BeO, Al_2O_3, 6SiO_2$, or $Be_3Al_2Si_6O_2$, which, in its rough opaque form, is called *beryl*; when purer and transparent it is either of a pale sea-green colour: *aquamarine*, or else of a bright green: *emerald*, both of which varieties have considerable value as precious stones. It further occurs as silicate simply in the mineral *phenakite*: $2BeO, SiO_2$, or $Si(O_2Be)_2$, and as double oxide of aluminium in *chrysoberyl*: BeO, Al_2O_3.

The metal may be obtained by leading the vapour of the chloride over fused sodium contained in steel boats, and afterwards washing with water. It is a white metal like aluminium, with a specific gravity of 1·85, and melts at a red-heat under partial oxidation. It is without action on water at the ordinary temperature, but decomposes it slowly on boiling. Dilute hydrochloric or sulphuric acid easily dissolves it with rapid evolution of hydrogen. Concentrated nitric acid scarcely acts on it. It dissolves also in the caustic alkalies (not in ammonia), forming soluble compounds resembling the aluminates.

Beryllium Oxide or *Beryllia*: BeO, is a white amorphous powder of 3·0 specific gravity, obtained by heating

Beryllium Hydrate: $Be(OH)_2$.—This compound is thrown down as a white gelatinous precipitate when ammonia is added to a solution of a beryllium salt. The precipitate forms a white powder when washed and dried; it is soluble in caustic potash or soda and in ammonium carbonate, from which solution it is again precipitated on boiling as a carbonate.

The salts of beryllium possess a pure sweet taste, whence the name *glucinum*, which is sometimes given to the metal; they are mostly soluble in water.

Beryllium Sulphate: $(SO_2)O_2Be + 4H_2O$, easily crystallizes when its aqueous solution is evaporated down. It forms a double compound with potassium sulphate, which is difficult to obtain in the crystalline form, and has a different composition to common alum, with which it is therefore not isomorphous.

Beryllium Chloride: $BeCl_2$, is prepared like aluminium chloride, which it resembles, but is less volatile. It forms, when pure, white, crystalline, highly deliquescent needles.

Beryllium Carbonate.—On adding sodium carbonate to a solution of a beryllium salt a precipitate of a basic carbonate is produced, which dissolves with difficulty in an excess of the reagent. This carbonate is much more easily soluble in ammonium carbonate, a fact which enables us to detect beryllium and to separate it from aluminium. Water containing carbonic acid also slightly dissolves the basic carbonate.

From the above properties of beryllium and its compounds it will be seen that the metal occupies a peculiar position between magnesium and aluminium, both of which it resembles in some points. It has long been a matter of discussion whether the element should be classed with the alkaline-earths or with the earths. In the former case it would be a diad with an atomic weight of 9·1, and its oxide would be written: BeO; in the latter the element is a triad, its atomic weight is half as much again, or 13·6, and its oxide becomes: Be_2O_3. Recently the specific heat of the metal has been determined (at 400°) and found to be 0·62. If this number is multiplied by the smaller atomic weight (9·1) it gives 5·6, proving, according to Dulong and Petit's law (p. 70), that this is the true atomic weight.

METALS OF THE EARTHS.

The chief representative of these metals is *aluminium*,[1] but the group also includes a number of metals of less importance, and much less known—viz. *gallium* and *indium*; *yttrium*, *terbium*, *erbium*, and *ytterbium*; *cerium*, *lanthanum*, and *didymium*; *thorium* and *zirconium*. All these metals have a strong attraction for oxygen, but considerably less than the metals of the alkaline-earths. Their basic oxides are sesquioxides—except those of thorium and zirconium. Notwithstanding their strong attraction for oxygen, they appear to possess only a weak affinity for sulphur, and their sulphides (except that of indium) cannot be obtained in the wet way. If ammonium or sodium sulphide is added to a solution of one of their salts, a precipitate of the hydrate, not the sulphide, is produced, and sulphuretted hydrogen is set free :—

$$Al_2Cl_6 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3 + 6NH_4Cl + 3H_2S.$$

ALUMINIUM.

Chemical Symbol: Al.—*Atomic Weight*: 27·1.

This element is never found free in nature, but combined with oxygen and silica it is one of the chief constituents of the superficial layer of the crust of the earth. *Felspar*, *granite*, *mica*, and many other rock masses contain aluminium silicate. In combination with fluorine and sodium fluoride it forms the mineral *cryolite*.

Aluminium is a tin-white metal of specific gravity 2·6, tough, but malleable ; it may be rolled into thin sheets and drawn into fine wire. It melts at about 700°—*i.e.* at a higher temperature than zinc, but lower than silver ; it is not magnetic, but conducts an electric current better than iron. The metal remains unchanged in dry as well as in moist air, becoming covered with an extremely thin layer of oxide—even at its melting point it only oxidizes slowly. If, however, a large surface is heated in the air—*e.g.* a piece of aluminium foil in the lamp—it burns brilliantly.

Concentrated nitric acid does not act upon aluminium, but dilute sulphuric or hydrochloric acid dissolves it readily with copious

[1] The author includes chromium with these metals, but the editor prefers to place it after manganese. The editor has also made some slight alterations—with additions—in treating of the rarer of these metals.

evolution of hydrogen. It easily dissolves in a solution of caustic potash or soda, evolving hydrogen and producing soluble compounds of alumina and potash or soda. The molten alkalies do not act upon it, but when fused with potassium carbonate, carbon is reduced.

The strong affinity of aluminium for oxygen and the halogens makes its preparation somewhat difficult. Its oxide is not reduced when glowed with charcoal, nor when heated in a stream of hydrogen. It may, however, be easily prepared, either by the electrolysis of fused sodium-aluminium chloride : $2NaCl, Al_2Cl_6$, or by decomposing the chloride with sodium. The latter process can be carried out on a small scale by leading the vapour of aluminium chloride over fused sodium with a stream of hydrogen. After the violent reaction is over, the reduced aluminium is found under the fused sodium-aluminium chloride produced at the same time, if the sodium was not in excess.

On the large scale, aluminium is manufactured in the following manner. The double chloride of sodium and aluminium is first prepared by heating a mixture of alumina, common salt, and charcoal in a stream of chlorine. 100 parts of the sublimed double chloride are next mixed with 35 parts of sodium and 40 parts of cryolite (to serve as a flux), and heated on the hearth of a reverberatory furnace. The aluminium is thus reduced, and collects on the hearth under the fused slag.

The high tenacity of aluminium, its property of not rusting, like iron, in the air, and its low specific gravity, would make it an extremely useful metal could it be prepared in larger quantities and at a lower price than is at present the case. It is now little used, except for scientific purposes and for the manufacture of aluminium bronze.

We are only acquainted with one oxide of aluminium, and only with one compound with chlorine and the other halogens.

Aluminium Oxide, *Alumina* : Al_2O_3.—This compound occurs in nature in crystals belonging to the hexagonal system—partly transparent, of a blue or red colour (probably due to traces of cobalt and chromium) as the two precious stones, the *sapphire* and *ruby*—and partly less pure, as grey, usually opaque, crystals, called *corundum*. Crystalline alumina is distinguished by its hardness—next to the diamond it is the hardest substance known, and is, therefore, highly valued for grinding and polishing. For this pur-

pose massive crystalline alumina, called ***emery***, is used. Emery is found in some parts of Asia Minor, especially on the island of Naros, as well as in Massachusetts.

The oxide may be easily prepared as a white amorphous powder by glowing either its hydrate or its double sulphate with ammonium —called ammonia alum.

Like all sesquioxides, alumina is a weak base, and is not soluble in acids either in the natural or artificial form. It can only be brought into solution by fusion with acid potassium sulphate, or with alkaline hydrates or carbonates. Alumina forms salts not only with strong acids but also with strong bases, in which it plays itself the part of an acid. Some of these salts—*e.g.* those of potassium and sodium—are soluble in water, hence it follows that aluminium hydrate when separated from aluminium salts by caustic soda (or potash) dissolves in an excess of the reagent.

Alumina is infusible at the highest temperatures of our furnaces, but melts in the oxy-hydrogen flame to a colourless glass, which crystallizes on cooling. By the previous addition of minute quantities of potassium dichromate, artificial rubies may be thus obtained.

Aluminium Hydrate : $Al_2(OH)_6$, or $Al(OH)_3$.—This compound, occurring in nature as *hydrargillite* or *gibbsite*, is obtained as a white gelatinous precipitate when a soluble aluminium salt is precipitated with ammonia. The precipitate, which is difficult to wash, dries to a translucent mass, and afterwards forms a light, white amorphous powder, insoluble in water. When gently heated it loses two molecules of water and is changed into a hydrate of the composition : $\left\{\begin{matrix} AlO \cdot OH \\ AlO \cdot OH \end{matrix}\right.$ which is also found in the mineral kingdom as *diaspore*. *Bauxite* is a hydrate : $(Al, Fe''')_2O_3 + 2H_2O$, chiefly found in Ireland.

Aluminium hydrate is easily dissolved both by acids and alkalies (except ammonia). In both cases salts are produced, the alumina playing the part of base or of an acid. It possesses the property of uniting with organic colours and precipitating them from their solutions, and is, therefore, a valuable mordant. Calico and other stuffs, which do not themselves unite with the colours with which they are to be dyed, retain them firmly if impregnated with aluminium acetate—a salt which readily deposits aluminium hydrate. Organic colours precipitated with aluminium hydrate are termed *lakes*. Alumina and its compounds are thus largely used in dyeing.

Aluminium Salts.—Aluminium, as we have just mentioned, forms two classes of salts: those in which it plays the part of a base, and those in which it is an acid. The former are the common salts of aluminium; the latter are called *aluminates.* They are found in the crystalline form in nature, and can also be prepared artificially.

Two classes of aluminates are known, one in which the *aluminic acid* is tribasic,[1] and one in which it is dibasic. These two acids are simply the two hydrates: $Al(OH)_3$ and $\left\{\begin{matrix} AlO \cdot OH \\ AlO \cdot OH \end{matrix}\right.$ The naturally occurring aluminates (often called *spinelles*) belong chiefly to the latter class. The following are the more important of these salts.

Potassium Aluminate: $\left\{\begin{matrix} AlO \cdot OK \\ AlO \cdot OK \end{matrix}\right.$ and *sodium aluminate*: $Al(ONa)_3$,[1] are obtained by dissolving aluminium hydrate in caustic potash or soda, and separate out on evaporation or on the addition of alcohol. *Magnesium aluminate*—the mineral *spinelle*: $\left.\begin{matrix} AlO \\ AlO \end{matrix}\right\} O_2Mg$, *zinc aluminate*—*gahnite*: $\left.\begin{matrix} AlO \\ AlO \end{matrix}\right\} O_2Zn$, and *ferrous aluminate*—*iron-spinelle*: $\left.\begin{matrix} AlO \\ AlO \end{matrix}\right\} O_2Fe$, are aluminates occurring in nature.

Aluminium Sulphate: $(SO_2)_3O_6Al_2 + 18H_2O$.—The normal salt of the above composition is occasionally found in nature, and is prepared by dissolving aluminium hydrate in sulphuric acid, or commercially by acting on clay (aluminium silicate), with concentrated sulphuric acid. The mixture of aluminium sulphate and silicic acid obtained by the latter process is known in trade as *alum-cake.* The salt crystallizes from concentrated solutions in fine needles or plates, which deliquesce in the air. Besides the normal salt, numerous basic compounds are known. One of these is found in nature as the mineral *aluminite*, and has the composition: $(SO_2)_3O_6Al_2 + 4Al(OH)_3 + 3H_2O$.

Aluminium sulphate forms crystalline double salts with the sulphates of the alkalies, of thallium, and of silver. These double sulphates all crystallize in the regular system, and are all isomorphous with one another: they are called *alums.* The longest known of these compounds is *potash-alum*, potassium-aluminium sulphate: $\left.\begin{matrix} SO_2 \\ SO_2 \end{matrix}\right\} \begin{matrix} O_3Al \\ OK \end{matrix} + 12H_2O$, or $KAl(SO_4)_2 + 12H_2O$, to which

[1] It is doubtful whether other aluminates than those derived from $H_2Al_2O_4$ exist.

reference has been previously made (p. 336). It may, like all the other alums, be considered as a double sulphate of potassium and aluminium, and its formula would then be : $SO_2(OK)_2 + (SO_2)_3O_6Al_2 + 24H_2O$.

Potash-alum, of the above composition, crystallizes from its aqueous solution in large, colourless, and transparent regular octahedra, often combined with faces of the cube. If its warm solution is mixed with potassium carbonate (or hydrate) so that the precipitate at first produced is redissolved, the solution, which now contains a basic salt, deposits crystals of ordinary alum in the form of cubes, not octahedra. This is called *cubic alum.*

Alum possesses a sweet, astringent taste, has an acid reaction, and is easily soluble in water, especially warm. It is insoluble in alcohol. When the crystals are exposed to the air they become covered with a white opaque crust, which is said to be due to the formation of a basic salt from the ammonia of the air, and not to loss of water. If alum is heated it melts in its water of crystallization, and as the liquid loses water it becomes thicker and thicker and froths considerably. Finally, the anhydrous salt remains behind as a spongy mass, known in medicine as *burnt alum.*

Alum may be prepared directly from its constituents by mixing solutions of aluminium and potassium sulphates, and evaporating down. The aluminium sulphate used for the manufacture of alum is principally obtained in two different ways—either by treating kaolin or some other clay (aluminium silicate) with concentrated sulphuric acid, or by roasting alum-shale and extracting with water. The *alum-shale* does not contain aluminium sulphate ready formed, but consists of a shale (essentially solidified clay) mixed with small crystals of iron pyrites, and often with some combustible substances. When roasted in the air oxidation takes place, with the production of ferric oxide (or ferrous sulphate), sulphurous anhydride and sulphuric acid, the latter acid decomposing the aluminium silicate, forming aluminium sulphate. The mass is extracted with water, the requisite quantity of potassium sulphate added, and evaporated down to crystallize. Some varieties of alum-shale are so easily decomposed, and contain the iron pyrites so finely divided, that it suffices to moisten them with water and leave them exposed to the air for some time to effect the required decomposition.

The value of an alum for dyeing purposes is greater the less

the amount of combined iron it contains, because this substance spoils the colour. Alum particularly free from iron is prepared from a naturally occurring basic aluminium sulphate, called *alunite*. This substance is much less widely distributed in nature than alum-shale, and is chiefly found near Rome, in Tuscany, and Hungary. The alum prepared from it is known in trade as *Roman alum*. Alunite, which is insoluble in water, may be considered as a compound of one molecule of anhydrous alum united with two of aluminium hydrate, and is therefore represented by the formula: $\begin{matrix} SO_2 \\ SO_2 \end{matrix}\Big\} \begin{matrix} O_3Al \\ OK \end{matrix} + 2Al(OH)_3$. When gently heated, it yields water, insoluble alumina, and soluble potash alum. The last named compound is then extracted with water, and usually crystallizes in cubes.

If a solution of aluminium sulphate is mixed with one of sodium, ammonium, rubidium, cæsium or thallium sulphate, alums are produced of the same crystalline form as potash-alum and of analogous composition. An alum of silver has also been obtained. These different alums are distinguished by the names soda-, ammonia-, &c., alum. Formerly, large quantities of ammonia-alum were manufactured in England from the ammoniacal liquors of the gas-works; the manufacture has now almost entirely ceased, owing partly to the immense quantities of cheap potassium compounds obtained from the Stassfurt beds. Ammonia-alum cannot be distinguished from potash-alum in its external characters.

Besides the substitution of the potash by other monoxides, the alumina in alum may also be displaced by other sesquioxides without altering the shape or general character of the compounds; and alums can be prepared in which the aluminium is displaced by iron, manganese, or chromium respectively. These alums are known by the names of the triad metals which they contain, and have the following composition:—

Iron-alum . . . . $\begin{matrix} SO_2 \\ SO_2 \end{matrix}\Big\} \begin{matrix} O_3Fe \\ OK \end{matrix} + 12H_2O$.

Manganese-alum . . . $\begin{matrix} SO_2 \\ SO_2 \end{matrix}\Big\} \begin{matrix} O_3Mn \\ OK \end{matrix} + 12H_2O$.

Chrome-alum . . . . $\begin{matrix} SO_2 \\ SO_2 \end{matrix}\Big\} \begin{matrix} O_3Cr \\ OK \end{matrix} + 12H_2O$.

These alums are coloured: iron-alum usually violet, chrome-

alum, dark-green or purple. Like alum proper, the potassium can be displaced by other monad metals, and we are thus acquainted with more than twenty isomorphous compounds belonging to this class.

Aluminium Phosphate: $PO \cdot O_3Al + 4H_2O$.—The normal salt is deposited as a white gelatinous precipitate, when a solution of sodium phosphate is added to one of aluminium sulphate or of alum. It is easily soluble both in acids and alkalies (except ammonia). Various basic phosphates are known, among which is the mineral *wavellite*.

Aluminium Silicate: $(SiO)_3O_6Al_2$.—A silicate having this composition is thrown down as bulky precipitate on adding an excess of a hot dilute solution of aluminium sulphate to a neutral solution of sodium silicate. A salt of the composition : Al_2O_3, SiO_2 is found crystallized in the mineral kingdom as *andalusite* and *disthene*. In combination with other silicates, aluminium silicate is one of the most important constituents of the crust of the earth. Among these may be mentioned the *felspars* of which the composition has been already given (p. 272). The commonest of these is *potash-felspar* or *orthoclase* : $KAlSi_3O_8$; less common are *soda-felspar* or *albite*, of similar composition, and *lime-felspar* or *anorthite*. Most of the naturally occurring double silicates are anhydrous, but some—the *zeolites*—contain water. To this class belong the minerals *natrolite* and *analcime*, which are hydrated double silicates of aluminium and sodium. They belong to the few silicates which are decomposed by hydrochloric acid. The felspars and most of the other silicates are quite unacted upon by hydrochloric acid, and can only be decomposed by treatment with hydrofluoric acid, or by fusion with sodium (or potassium) carbonate.

One of the most important hydrated silicates is *clay*, which in its purest form is *kaolin* or *china-clay*. This is hydrated aluminium silicate of the approximate composition : $Al_2O_3, 2SiO_2 + 2H_2O$. It is produced by the gradual weathering of felspar, which is often found mixed with it. The process consists in a gradual change of the potassium silicate by the carbonic acid of the air into soluble potassium carbonate (see p. 344), leaving insoluble aluminium silicate, which then unites chemically with water.

Kaolin is largely used for the manufacture of *porcelain* and *earthenware*. Clay when finely powdered and mixed with water forms a plastic mass which readily allows itself to be moulded into various shapes, and if the clay is afterwards heated, it bakes together to a hard but porous mass It is because of these two properties that clay is so largely used for the manufacture of articles of china, stoneware, and earthenware. But vessels prepared from clay alone are porous, and cannot be used to contain liquids: to make them available for this purpose they are either coated with a thin layer of glass (the *glaze*), or else the clay is previously mixed with some fusible material (the *frit*), then burnt and glazed. In the manufacture of true *porcelain* the frit employed is usually either felspar or a mixture of felspar and quartz, which is carefully mixed with the kaolin and then burnt at a high temperature. In true porcelain, the frit penetrates through the entire mass—giving it its well-known translucent appearance. Porcelain is usually glazed by dipping it in finely powdered felspar suspended in water, and then again heating.

Stoneware of very various qualities is a coarser kind of porcelain made with a more easily fusible frit which does not penetrate through the entire mass of the clay. Stoneware is glazed with a more fusible glaze than felspar, such as stannic oxide or lead oxide.

Earthenware or *Fayence*, which is made from variously coloured clays, is porous, and of a yellow or reddish colour. It is glazed either with lead oxide, forming an easily fusible lead silicate, or with common salt. The salt is usually thrown into the kiln when the burning is nearly over. It then volatilizes, and is decomposed with the water-vapour present and the silica of the clay, forming hydrochloric acid and a sodium silicate, which acts as a glaze.

A clay rich in calcium carbonate, and which is sometimes mixed with clay in making earthenware, is known as *marl*. Intimate mixtures of clay with ferric oxide of various colours from yellow to brown are used as pigments under the name of *ochres*. *Fuller's earth* and *bole* are fine clays used for cleansing clothes and other purposes.

Ultramarine.—The highly valued ornamental stone called *lapis lazuli*, and occurring especially in China and Thibet, was previously powdered and sold under the name of *ultramarine* for its weight in gold. This substance is essentially a compound of

sodium and aluminium silicates with sodium pentasulphide. Fifty years ago Gmelin discovered a method for the artificial manufacture of ultramarine, and since then his processes have been so perfected (by C. Leverkus, 1834, and others), that the artificial substance can now be made of a finer colour than that found naturally. This discovery has, therefore, been well described as one of the most brilliant victories of chemical science during the present century.

The artificial preparation of ultramarine appears at first extremely simple, but in order to prepare a pigment of fine colour a number of practical details must be attended to. These can only be acquired by long experience, and are often preserved as trade secrets.

Ultramarine is obtained by heating clay in a closed crucible with some mixture which produces sodium sulphide, such as sulphur and sodium carbonate, or sodium sulphate and charcoal. The product first produced is green—*ultramarine-green*—but if mixed with sulphur and again gently heated, changes to the well-known blue colour of ultramarine proper. The change in colour is probably due to the formation of a polysulphide of sodium. If heated too strongly, the colour is destroyed.

The chemical constitution of ultramarine is still uncertain. It is thought that the blue compound contains sodium pentasulphide, and the green the disulphide. The sodium sulphide cannot be displaced by potassium sulphide. The products are finely ground, brought into trade in various tints, and largely used for many purposes.

Ultramarine is not so permanent as smalt (cobalt blue), nor as indigo, but is not decomposed by soaps and alkalies like Prussian blue. Acids, however, at once decompose ultramarine, and it may be recognized by the reaction that when mixed with hydrochloric acid, sulphuretted hydrogen is evolved, much white sulphur separates—from the sodium pentasulphide—and the blue colour entirely disappears.

Aluminium Chloride: Al_2Cl_6.—This compound may be obtained by burning the metal in a stream of chlorine. It is, however, usually prepared by intimately mixing alumina and powdered charcoal (best sugar charcoal[1]) with starch paste, and then proceeding as described under the preparation of silicon tetrachloride (see p. 273). On glowing in a stream of dry chlorine,

[1] Or a very pure form of lamp-black, known as *gas-black*.—ED.

aluminium chloride sublimes in yellowish crystalline plates. The yellow colour is due to traces of ferric chloride, which may be removed by sublimation over hot aluminium, when the volatile ferric chloride is converted into non-volatile ferrous chloride. Pure crystalline aluminium chloride is colourless, sublimes when gently heated, and rapidly attracts water from the air.

The aqueous solution of the chloride, which may be obtained by dissolving aluminium hydrate in hydrochloric acid, when evaporated down deposits colourless deliquescent crystals of the composition: $Al_2Cl_6 + 12H_2O$. The water cannot be expelled from these crystals by heating so as to leave the anhydrous chloride, because the aluminium chloride is then decomposed with the formation of hydrochloric acid, and a basic chloride or even alumina. Aluminium chloride unites with sodium and other chlorides, producing fairly stable double salts.

Aluminium Fluoride: Al_2F_6, is obtained by dissolving aluminium hydrate in hydrofluoric acid, or by glowing a mixture of alumina and fluor-spar in hydrochloric acid gas. It is insoluble in water, sublimes at a high temperature in colourless cubes, and in combination with sodium fluoride forms the mineral *cryolite*: $Na_3AlF_6 = 6NaF,Al_2F_6$.

Aluminium Sulphide: Al_2S_3, is produced when alumina is glowed in the vapour of carbon disulphide. It is a bright yellow vitreous mass, which with water, or even moist air, rapidly decomposes into sulphuretted hydrogen and aluminium hydrate.

Detection of Aluminium Compounds.

Aluminium salts are distinguished from those of the alkalies and alkaline earths by the production of a white gelatinous precipitate of aluminium hydrate with ammonia—a precipitate which is insoluble in ammonium salts and is therefore produced in their presence (comp. magnesium). They are further distinguished by yielding a white precipitate of aluminium hydrate, not sulphide, with ammonium sulphide.

Like all sesquioxides, alumina is a weak base, and does not form compounds with weak acids—*e.g.* carbonic acid. If a solution of aluminium chloride is mixed with one of sodium carbonate, aluminium hydrate and sodium chloride are formed, and carbonic acid set free. If the sodium carbonate is in excess, acid sodium

carbonate is produced. The weak basic properties of alumina are further shown by its behaviour with caustic soda (or potash). Caustic soda precipitates aluminium hydrate from solutions of aluminium salts, but the precipitate dissolves in an excess of the alkali, forming sodium aluminate—a salt in which alumina plays the part of an acid (p. 424). Aluminium compounds when heated on charcoal before the blowpipe leave a white infusible mass, which, when moistened with a drop of cobalt nitrate and again heated becomes of a fine blue colour.

GALLIUM.

Chemical Symbol: Ga.—*Atomic Weight*: 69·8.

This element is contained in some samples of blende found in the Pyrenees, but only in extremely minute quantities (about 0·002 per cent.) Its spectrum contains two characteristic lines in the violet which led to its discovery by the French chemist, Lecoq de Boisbaudran in 1875.

Gallium is a white lustrous metal of low melting-point (30°) when once melted it remains liquid, like mercury, even at 0°. Its specific gravity is 5·9. The metal remains unaltered in the air, and only becomes covered with a thin layer of oxide when heated nearly to redness. It is not attacked by water at the ordinary temperature, but dilute hydrochloric acid as well as the alkalies dissolve it with evolution of hydrogen.

The compounds of gallium resemble those of aluminium. *Gallium oxide*: Ga_2O_3 and the hydrate are white amorphous powders, insoluble in water. *Gallium chloride*: Ga_2Cl_6, which may be obtained by heating the metal in a stream of dry chlorine, is soluble in water and easily sublimes. A dichloride: $GaCl_2$ is also known.

Ammonium-gallium alum: $\left.\begin{matrix}SO_2\\SO_2\end{matrix}\right\}\begin{matrix}O_3Ga\\ONH_4\end{matrix} + 12H_2O$, crystallizes in regular octahedra.

INDIUM.

Chemical Symbol: In.—*Atomic Weight*: 113·7.

Indium, like gallium, belongs to the rarest metals; it is also found in very small quantities in some zinc ores, and when these are worked for zinc alloys itself with this metal. The zinc from Freiberg in Saxony contains from 0·05 to 0·1 per cent. of indium. If such zinc is treated with insufficient hydrochloric acid to completely dissolve it, the indium remains behind with other metals, and is purified by different processes.

Indium is a white lustrous metal, of specific gravity 7·4, and melting at 176°. It dissolves slowly in hydrochloric or dilute sulphuric acid, but easily in nitric acid. The metal remains unchanged in the air, but burns, when heated to redness, with a violet light, and producing brown vapours. Indium is a triad in all its compounds.

Indium Oxide: In_2O_3, is a bright yellow powder, which becomes dark brown when heated.

Indium Hydrate: $In(OH)_3$, is thrown down from indium salts on addition of ammonia, as a white gelatinous precipitate, resembling aluminium hydrate; it also dissolves in caustic soda or potash.

Indium Sulphate: $(SO_2)_3O_6In_2$, remains as a gummy mass when its solution is evaporated down. It unites with ammonium sulphate, but not with potassium sulphate, and forms ammonium-indium alum: $\begin{matrix} SO_2 \\ SO_2 \end{matrix}\Big\} \begin{matrix} O_2In \\ ONH_4 \end{matrix} + 12H_2O$.

Indium Chloride: $InCl_3$, is prepared by heating either the metal or a mixture of the oxide and charcoal in a stream of dry chlorine, when it sublimes in white crystalline plates. It is very deliquescent.

Indium Sulphide: In_2S_3, is produced when indium and sulphur are gently heated together, and then forms a brown infusible mass. Sulphuretted hydrogen precipitates the same compound from neutral solutions of indium salts, or when sodium acetate has been added to the solution. In the presence of free hydrochloric acid no precipitate is obtained. Indium, which is otherwise closely allied to aluminium and gallium, in this respect resembles zinc.

Traces of an indium compound, if introduced in the non-luminous gas flame, may be at once detected by its spectrum,

which is characterized by one line in the dark blue. It was this line which led to the discovery of the metal, and from which it derives the name.

SCANDIUM, YTTRIUM, TERBIUM, ERBIUM, and YTTERBIUM.

Chemical Symbols: Sc, Y, Tr, Er, Yb.
Atomic Weights: 44, 89 (?), 148, 166, 173.

These five rare elements, which have not yet been prepared in the free state, are only found in a few extremely scarce minerals—*e.g.* in *gadolinite* as silicates, in *yttrotantalite* and *samarskite* as tantalates and niobates.

The *oxides* of scandium, yttrium, and ytterbium: Sc_2O_3, Y_2O_3, and Yb_2O_3, are white, terbium oxide: Tr_2O_3, is yellow, and erbium oxide: Er_2O_3, pink.

The salts of all four so closely resemble one another that they can only be partially separated with considerable difficulty. The *sulphates* and *nitrates* are soluble in water, the former compounds being more soluble in cold than hot water. The *chlorides* are non-volatile, and can be prepared anhydrous like magnesium chloride. Finally, the *oxalates* and *carbonates* are insoluble, so that they can be separated from aluminium and iron (in the ferric state) by precipitating with oxalic acid.

The salts of erbium are of a pink colour, and yield a very characteristic absorption spectrum, by means of which small quantities of the element may be detected.

CERIUM, LANTHANUM, and DIDYMIUM.

Chemical Symbols: Ce, La, Di.
Atomic Weights: 140·3, 139 (?), 146 (?).

These three elements, which may be prepared by the electrolysis of their fused chlorides, always occur associated with one another in nature—usually as a hydrated silicate: *cerite*, which is decomposed by hydrochloric or sulphuric acid.

Cerium forms two *oxides*—viz. a sesquioxide: Ce_2O_3, and a peroxide: CeO_2. Both are white compounds, but the latter becomes

yellow when heated in the air. The two other oxides, lanthanum oxide : La_2O_3, and didymium oxide : Di_2O_3, correspond to the sesquioxide of cerium. Didymium also forms a brown peroxide.

The *salts* of the three metals resemble one another so closely that it is difficult to separate them. The cerium may be got rid of as the peroxide when the alkaline solution containing cerium hydrate in suspension is acted on by chlorine, but the separation of lanthanum and didymium is much more difficult.

The *sulphates*, *nitrates*, and *chlorides* closely resemble those of the preceding group. The *oxalates* are also insoluble in water and dilute acids. The sulphates are distinguished by forming a double sulphate with potassium (not an alum), which is quite insoluble in a saturated solution of potassium sulphate, and so enables us to separate this group of metals from the preceding group.

Didymium compounds are pink, like those of erbium, but with a bluer tinge. They also yield a characteristic absorption spectrum, of which the darkest band is one in the yellow. They have been decomposed into distinct, though similar, substances, which differ from one another mainly in their absorption spectra. *Hence that which has been heretofore considered to be elementary didymium is not really homogeneous.*

THORIUM.

Chemical Symbol: Th.—*Atomic Weight*: 232·5.

This extremely rare element is found in some copper ores and in two scarce minerals, of which both are silicates—the one anhydrous, called *thorite*, and the other hydrated, *orangite*.

The metal can be extracted by acting on its volatile *chloride*: $ThCl_4$, with sodium. The only *oxides* yet described are: ThO_2 and Th_2O_7. Its *sulphate*, *chloride*, and *nitrate* are all soluble in water.

ZIRCONIUM.

Chemical Symbol: Zr.—*Atomic Weight*: 90.

Zirconium is also one of the rarer elements, and chiefly found in its silicate, the minerals *zircon* and *hyacinth*: $Si(O_4Zr)$. The metal is obtained in brilliant brittle scales, by strongly heating potassium fluozirconate with aluminium in a graphite crucible, and afterwards extracting the excess of aluminium with hydrochloric acid. It has a specific gravity of 4·1, is very difficultly fusible, and is not attacked by oxygen at a red heat, but burns in the oxy-hydro-

gen flame. Hydrochloric, nitric, or sulphuric acid scarcely attacks it, but it dissolves in hydrofluoric acid with evolution of hydrogen.

The mineral zircon is not attacked by any acid, but is decomposed by fusing it either with sodium carbonate, or, better, with acid potassium fluoride; in the latter case potassium fluosilicate and fluozirconate are formed, of which the latter dissolves when the fused mass is boiled with water, while the former remains undissolved. From this solution ammonia precipitates

Zirconium Hydrate: $Zr(OH)_4$, as a white voluminous mass, which loses water when heated, and leaves *zirconium oxide* or *zirconia*: ZrO_2, as a white powder, insoluble in dilute acids. Caustic soda also precipitates the hydrate, which is soluble in an excess of this reagent, like aluminium and beryllium hydrates.

Zirconium Sulphate: $\left.\begin{matrix} SO_2 \cdot O_2 \\ SO_2 \cdot O_2 \end{matrix}\right\} Zr$, obtained by dissolving the hydrate in sulphuric acid, crystallizes with difficulty from its aqueous solution.

Zirconium Chloride: $ZrCl_4$, prepared like aluminium chloride, by glowing a mixture of zirconia and charcoal in dry chlorine, is a white crystalline substance, volatile without decomposition, and soluble in water. The same solution is obtained by dissolving zirconium hydrate in hydrochloric acid, from which, however, an *oxychloride*: $ZrOCl_2$, with varying quantities of water, crystallizes in colourless silky prisms on concentration. *Zirconium fluoride*: ZrF_4, sublimes as a colourless crystalline mass when an intimate mixture of powdered zircon and fluor-spar is heated in a stream of hydrochloric acid. It is insoluble in water and hydrochloric acid, but dissolves in hydrofluoric acid. On mixing this solution with potassium fluoride and evaporating down, crystals of potassium fluozirconate: $ZrF_4 + 2KF$, or K_2ZrF_6 are obtained, isomorphous with the corresponding compounds of silicon, titanium, and tin.

Zirconium (like thorium) is a tetrad in nearly all its compounds; it is connected with silicon and titanium on the one hand, and with tin on the other, as is readily seen from the above description of its compounds.

GERMANIUM. (See Appendix.)

Chemical Symbol: Ge.—*Atomic Weight*: 72·3.

HEAVY METALS.

IRON.

Chemical Symbol: Fe.—*Atomic Weight*: 56.

Iron belongs to the most widely distributed, and to the most important elements. It is found in the free state in meteorites —larger or smaller masses of iron which occasionally reach the earth from extra-terrestrial space. The meteorites always contain nickel, often as much as 10 per cent., and may be distinguished from metallic iron of other origin by peculiar markings (first noticed by Widmanstädt) which are produced when the surface is polished and treated with nitric acid.

The most important compounds of iron are its oxygen compounds; these are used exclusively for the extraction of the metal. They are not only very widely distributed, but are often found in immense quantities. Among these are: *specular-iron*, ferric oxide: Fe_2O_3, beautifully crystallized in the hexagonal system, and especially abundant on the Island of Elba. Ferric oxide, as granular, columnar, or earthy masses forms the important ore, *red hæmatite*, which when combined with water is known as *brown hæmatite* or *limonite*. Red hæmatite is principally found in Lancashire and Cumberland in England, while brown hæmatite is found either associated with carboniferous rocks in the Forest of Dean and Glamorganshire, or else with oolitic rocks, as the earthy hæmatite of Northamptonshire and Lincolnshire. The *bog iron-ores* of Ireland and North Germany also consist of limonite, but of a much more recent date. *Magnetic iron ore*: Fe_3O_4, when pure, is one of the most valuable of iron ores. It is found crystalline, but usually in rough masses or as sand, and is the chief ore from which the Swedish iron is extracted. *Spathic iron ore* or *siderite* is impure ferrous carbonate: $CO \cdot O_2Fe$, and is found in small quantities as such in England, but chiefly occurs in some German localities, and in Styria. Spathic iron ore is generally found in England, intimately associated with clay as *clay ironstone*, or *argillaceous iron ore*—one of the most important, if not

he most important English ores of iron. It occurs in large quantities in various parts ot the kingdom.

Other compounds of iron which are found in large quantities in nature but which cannot be used as iron ores are: *Iron pyrites*: FeS_2, distinguished by its bright yellow colour and the readiness

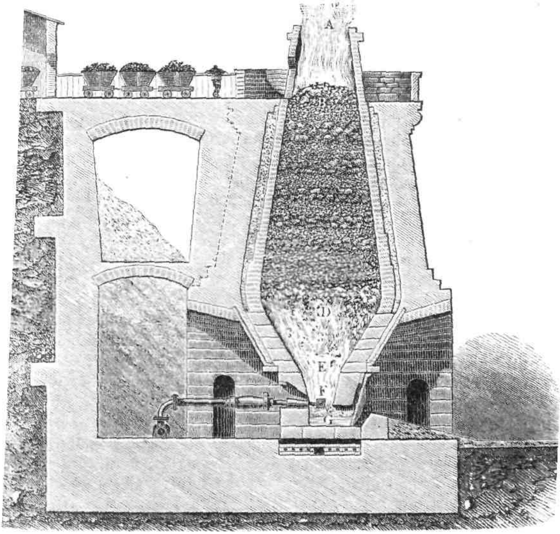


Fig. 65.

with which it crystallizes; *magnetic pyrites*: Fe_3S_4 or Fe_7S_8, richer in iron; *copper pyrites*: $CuFeS_2$; *arsenical pyrites*: FeAsS, &c.

Iron is extracted from its ores by reduction with carbon at a high temperature. The furnaces used for iron smelting, called *blast-furnaces*, are usually built in the form represented in fig. 65. They are of strong masonry, lined with fire-bricks, and reach a height of sixty or eighty feet. The iron ore, which if clay iron ore

must first be roasted to expel carbonic acid and water, is introduced at the top with alternate layers of coke, or in some countries (Sweden) charcoal. And if the ore does not contain the requisite constituents to form a fusible slag, either limestone or silica in some form must be added for this purpose. At the lower part of the furnace a blast of air is blown in from several iron openings, called *tuyères*, which are kept at a low temperature by a stream of cold water circulating through them. Above the blast about D in the figure, the iron is reduced to a spongy mass, partly by the hot carbonic oxide, and partly by the free carbon. This reduced iron takes up carbon &c. in its descent, becomes more fusible, and finally forms a liquid mass on the hearth at G. At the same time the silica, lime, alumina &c. unite to form a fusible slag (p. 404), which is lighter than the iron, and by floating on its surface protects it from the oxidizing action of the blast. When the furnace is at work, a continuous stream of molten slag flows out by a side opening—over a raised portion—the *dam-plate* (not shown in the figure). The inflammable gases which escape from the top of the furnace consist chiefly of carbonic oxide, produced by the reduction of the carbonic acid, and of nitrogen. In modern furnaces these gases are not allowed to burn in this wasteful manner at the mouth of the furnace, but pass out at a side opening near the top, and are then used to heat the blast of air entering at the base of the furnace. A large economy of fuel is effected by using a hot instead of a cold blast. In such furnaces, the top is closed with a valve arrangement (*cup and cone*) through which the materials are introduced when necessary. At stated intervals, when sufficient molten iron has collected on the hearth G, a hole at the base, which is closed with sand or clay, is opened with a long iron rod, and the iron flows out into rough sand moulds, producing rough bars—called *pigs*. Such a furnace is kept in continuous action for several years.

Cast-iron obtained in this way is still very impure; it may be purified from the slag which it contains by remelting with a suitable flux. Even then it contains small quantities of sulphur, phosphorus, and of silicon reduced from the slag, as well as from 3 to 5 per cent. of carbon, partly as graphite and partly in chemical combination with the iron. Two varieties of cast-iron are distinguished—viz. *white cast-iron* and *grey cast-iron*. The former is generally produced when the temperature of the furnace is low, and when the metal is rapidly cooled. It contains

the whole of its carbon combined with the iron, is silver white in colour, whiter than pure iron, and exhibits a lamellar, crystalline fracture. The latter variety—grey cast-iron—is produced with a high temperature and slow cooling, and contains 0·6 to 1·5 per cent. of its carbon combined with the iron, the rest (2·9 to 3·7 per cent.) being in the free state, as in the state of graphite. Grey cast-iron is darker in colour than white iron, and has a granular crystalline fracture. *Mottled cast-iron* is an intermediate variety between these two forms. When cast-iron is dissolved in dilute hydrochloric acid, the carbon present as graphite remains behind, while that in chemical combination with the iron combines with the nascent hydrogen, and forms volatile hydrocarbons. *Spiegel-eisen* and *ferro-manganese* are varieties of cast-iron containing manganese, and are largely used for the manufacture of steel.

Cast-iron melts at a lower temperature than any other form of the metal, but is brittle, and cannot be worked up into any shape. It is, therefore, only used for those articles which can be cast in moulds. But as the percentage of carbon diminishes the malleability increases, and the iron becomes more difficultly fusible. Iron containing the smallest quantity of carbon (not more than 0·5 per cent.) is called *wrought-iron*, while intermediate between wrought- and cast-iron are the various kinds of *steel*. In order, therefore, to convert cast-iron into wrought-iron it is necessary to abstract the greater part of the carbon which it contains. This is done by two processes, both depending on the same principle, called *puddling* and *fining*. In the former process, which is most generally used in England, the crude pig-iron is melted with slags rich in ferric oxide on the hearth of a reverberatory furnace with side openings. A considerable quantity of its silicon and carbon is removed by contact with the hot air blowing over it, and by the oxygen of the slag. Long iron bars are then inserted by the workmen at the side doors, and the molten metal stirred and worked up so as to expose it still further to the oxidizing action of the air. As the process goes on, the iron gradually becomes more difficultly fusible, and at last forms a tough mass, in which state it is removed from the furnace and hammered to remove the fusible slag which it still contains. It is then further hammered or rolled into bars or plates.

In the process of *fining*, the cast-iron is first melted on a hearth, and then a blast of air blown through it from several tuyères. A portion of the iron is oxidized to the magnetic oxide, and nearly

the whole of the carbon and silicon is removed. After the mass has become pasty it is worked, like puddled iron, by hammering and rolling.

Wrought-iron prepared in either of these ways is never quite free from carbon, but only contains from 0·1 to 0·5 per cent. Traces of silicon are also usually present, and, what is of more importance, traces of sulphur and phosphorus. Iron containing even a small quantity of sulphur is brittle when hot, or is said to be *red-short*, while that containing phosphorus to the extent of more than a half per cent. is brittle when cold, or, as it is said, is *cold-short*.

Wrought-iron has a pale grey colour, is very tenacious, ductile, and malleable. Its specific gravity is about 7·8. At a red-heat it becomes pasty, and can then be readily welded together and fashioned into various shapes. When two pieces of iron are to be welded together, the smith makes them both red hot in the forge, sprinkles them with sand, and then unites them into one solid piece by hammering. Without the addition of sand or some such substance (borax), the two surfaces of iron would be unable to unite with one another, because of the layer of oxide with which they become coated when heated in the air. The silica of the sand combines with the iron oxide, forming an easily fusible slag, which is removed by hammering, leaving the two surfaces of bare metal, which unite together under the pressure of the blows.

Wrought-iron, during its process of manufacture, acquires a fibrous structure, which greatly increases its resistance to breaking or tearing. It is on account of this property that wrought-iron is used for so many purposes for which brittle cast-iron, with its crystalline, granular structure, is unsuitable. An axle of a wheel, for example, if made of cast-iron, would break after a few turns on a rough road, but one of wrought-iron stands for years; and if it occasionally happens that an axle of a railway carriage breaks, it is always found that the fibrous wrought-iron has gradually become granular and crystalline by the long-continued vibrations.

Steel is a modification of iron intermediate between cast- and wrought-iron both in its properties and composition, as far as carbon is concerned. Hard steel contains 1·4 to 1·6 per cent. of combined carbon; it unites the hardness and fusibility of cast-iron with the ductility and malleability of wrought-iron. Steel can be produced either from wrought- or cast-iron. Up to the year 1856 the only known method of obtaining steel was by imbedding bars of wrought-iron in charcoal-powder contained in closed cast-iron

boxes, and then heating to bright redness for about a week or longer. By this process carbon is gradually taken up by the iron in some unknown manner, and the latter becomes completely converted into steel. The process is called *cementation*, and the product *cement-steel*. Cement-steel can be rendered more uniform in structure by working under the hammer at a red-heat, or by fusing and casting into blocks. It then forms what is called *cast-steel*.

Steel can now be much more economically obtained directly from cast-iron. Two processes are chiefly employed to effect this change—known as the Bessemer and Siemens-Martin processes respectively. In the *Bessemer* process five to ten tons of cast-iron are fused and poured into the *converter*—a large egg-shaped vessel lined with fire-clay, with a narrow mouth and with an opening at the base through which air can be blown. A current of air is then blown through the molten metal, which oxidizes nearly the whole of the carbon and silicon. As soon as this point is reached the blast is stopped, a small quantity of spiegeleisen is added to impart carbon and manganese, and the metal at once run into moulds. If the cast-iron employed for making Bessemer steel contains sulphur and phosphorus, these impurities are not removed when a converter with the usual lining of siliceous fire-clay is used; they remain in the steel. It was, however, discovered that if the lining of the converter contains free lime, this substance unites with the sulphur and phosphorus, when oxidized by the air, and a steel free from these impurities is obtained. Steel is also made from cast-iron by the *Siemens-Martin* process, which consists in fusing cast-iron in a specially constructed furnace, and adding wrought-iron to it until the requisite composition has been obtained. Some spiegeleisen is then added as in the Bessemer process, and the steel cast into moulds. Mild steel made by these two processes contains 0·15 to 0·4 per cent. carbon.

Steel is of a pale grey colour and takes a high polish. It is more easily fusible than wrought-iron, and its structure is finely granular, not fibrous, in consequence of which it is more brittle than wrought-iron. Steel is especially distinguished from wrought-iron by its hardness, which it especially acquires when heated to redness and rapidly cooled in water; it is then also exceedingly brittle and highly elastic. *Glass-hard steel*, *i.e.* steel hardened in this way, has but few uses: in order to adapt the steel to the wants of daily life it must be toughened or *tempered*. This is done by again heating and again rapidly cooling, and the higher the temperature

of the second heating (up to a dull red-heat) the tougher and less hard the steel. If the steel is polished it gradually becomes covered with a thin coating of oxide, the colour of which varies from a pale yellow to a dark blue, according to the temperature (240° to 300°) to which it has been heated. Cutting tools of various kinds are tempered in this way according to the purpose for which they are to be used. The specific gravity of steel is less after hardening (7·6) than it is before (7·8).

The preparation of chemically pure iron in the compact state is exceedingly difficult, if not impossible. If pure iron is fused in a crucible of gas-carbon it combines with some of the carbon; if in one of porcelain, it reduces small quantities of silicon and aluminium with which it unites chemically; and approximately pure iron can only be obtained by fusing in a lime crucible with the oxy-hydrogen blowpipe. Pure iron in the form of a powder may be obtained by reducing pure ferric oxide or ferrous chloride in a stream of hydrogen. It then remains as a dark grey powder (*reduced iron*), which is so finely divided that it takes fire in the air, unless it has been strongly heated in the stream of hydrogen.

Iron in all its forms is strongly attracted by the magnet: we say it is *magnetic*. Its magnetic power far exceeds that of any other substance. Soft iron becomes magnetic when brought near a magnet, but loses its magnetism as soon as the magnet is removed. Steel, on the other hand, does not so readily become magnetised, but retains its magnetism for some time. Artificial magnets are made of straight or curved steel bars by rubbing them with other magnets.

Notwithstanding the strong attraction of iron for oxygen, the metal remains unchanged in dry air and oxygen, but moist air, and especially water containing dissolved air, gradually oxidizes it —we say, the iron rusts. A drop of water placed on a polished strip of iron and allowed to evaporate leaves behind a dull reddish stain of oxide—*iron-rust*. This rust is not the oxide but the hydrate, and is produced by the simultaneous action of the oxygen and the water. Ferric hydrate produced in this way can unite chemically with ammonia and carbonic acid; iron-rust which has been long exposed to the air gives off these substances when heated.

Many metals which, like zinc, rust in the air, are protected from further oxidation by the compact layer of oxide which is first pro-

duced. But in the case of iron the layer of rust is less compact, and the process goes on, comparatively quickly, until the whole of the metal is oxidized. For this reason sheet iron cannot be used to protect the roofs of houses, but zinc or lead must be employed instead. Iron may be protected from rusting by coating it with a layer of some metal which oxidizes slowly in the air, such as tin (*tin-plate*), zinc (*galvanized iron*), or lead (*terne-plate*). The process in all cases consists in dipping the clean iron plates into the molten metal, and has nothing to do with electricity. Another process employed for rendering iron articles proof against rust consists in coating them with a layer of the magnetic oxide. For this purpose, the articles are heated to redness in a current of steam, a portion of which oxidizes the surface of the iron while hydrogen is set free. It has also been found that iron does not rust in water which has been made feebly alkaline by sodium carbonate.

Iron is the most valuable of all metals ; it is more valuable than gold, because its properties in its varied forms as cast-iron, wrought-iron, and steel, make it applicable to so many useful purposes for which no other metal can be used. And it has been well said that without iron there would be no civilization. The metal would be still more valuable if some simple means were known by which it could be converted into a passive state, and, like platinum, remain unchanged in the air and in water containing air. Such a discovery would completely revolutionize many branches of industry. We can actually produce this change in the properties of the metal, but only temporarily. A rod of iron dipped into red fuming nitric acid becomes thus *passive*, and now no longer dissolves in ordinary nitric acid, nor rusts in the air. But if touched or scratched with a piece of ordinary iron it loses these peculiar properties at once. The problem of how to make this passive state permanent remains as yet unsolved.

At a red-heat iron is more rapidly oxidized than by moist air at the ordinary temperature. A red-hot rod of iron becomes covered with a coating of oxide, which falls off when the iron is hammered on the anvil by the smith. This *scale*, as it is called, consists essentially of the magnetic oxide : Fe_3O_4, and forms black, dull scales when cold. The particles of iron which fly off and burn as sparks when a flint and steel are struck together, also form the same oxide, and the fused nodules produced when steel burns in oxygen (p. 14) have the same composition.

Red-hot iron absorbs considerable quantities of carbonic oxide,

which it parts with to the air when in contact with it. This happens, for example, when iron stoves are heated to redness. And the injurious action of such stoves when too strongly heated is largely due to the carbonic oxide which then diffuses into the air of the room.

Iron filings produced by the mechanic in working up iron articles are largely used for a number of purposes, owing to the larger surface which they expose to the action of various liquids than larger pieces of the metal. Many compounds of iron are prepared from them, and considerable quantities are employed for the commercial reduction of nitrobenzol to aniline in the presence of acetic acid. Iron in the state of a fine powder (*reduced iron*) is produced, as previously stated, by reducing finely divided ferric oxide in a stream of hydrogen.

Iron is attacked and dissolved by nearly all acids; dilute sulphuric, hydrochloric, or acetic acids dissolve it, with evolution of hydrogen, producing ferrous sulphate, chloride, or acetate respectively. Ordinary concentrated nitric acid dissolves iron, with the formation of ferric nitrate and lower oxides of nitrogen. Very dilute nitric acid dissolves it, like sulphuric acid, but the hydrogen is not set free; in its nascent state it gradually reduces some of the nitric acid to ammonia. That the solution contains ammonium nitrate as well as ferrous nitrate, may be readily proved by the ammonia evolved when it is mixed with caustic soda.

COMPOUNDS OF IRON.

Iron occurs in nearly all its compounds as a diad and triad (or tetrad) element. It is a diad in the *ferrous compounds*, ferrous oxide: FeO, ferrous chloride: $FeCl_2$, &c., and a triad (or tetrad) in the *ferric compounds*—ferric oxide: Fe_2O_3, ferric chloride: Fe_2Cl_6, &c. Ferrous oxide and ferric oxide both possess basic properties; the latter, like all sesquioxides, is a weak base—weaker than ferrous oxide. It is more stable than ferrous oxide as it is not changed by the oxygen of the air. A third oxide of iron is also known, containing more oxygen than ferric oxide, and having the properties of an acid. This *ferric acid*, probably $FeO_2(OH)_2$, appears only to exist in union with strong bases, and probably contains hexad iron, like sulphuric acid contains hexad sulphur.

FERROUS COMPOUNDS.

Ferrous Oxide : FeO.—Owing to the strong attraction of this compound for oxygen it is difficult to prepare, and has possibly never been obtained pure. It is produced, with some metallic iron, when ferrous oxalate is gently heated without access of air, or as a black glistening powder when the mixture of carbonic oxide and carbonic acid, obtained by heating oxalic acid with sulphuric acid (p. 295), is led over hot ferric oxide. The substance so obtained easily dissolves in hydrochloric or nitric acid, without evolving hydrogen, and when heated in the air is first oxidized to the magnetic oxide, and then to ferric oxide.

Ferrous Hydrate : $Fe(OH)_2$, is obtained as a white precipitate on mixing solutions of ferrous sulphate and caustic soda both free from air. In consequence of the readiness with which it attracts oxygen from the air, the white precipitate rapidly becomes green, and finally yields a brown mass of ferric hydrate. Ferrous hydrate dissolves in salts of ammonium, and is, therefore, not precipitated by ammonia from a solution to which ammonium chloride has been added.

Ferrous Sulphate, *Green Vitriol*: $SO_2 \cdot O_2Fe + 7H_2O$.—This is the best known salt of iron, and is that from which most of the other salts are prepared; it is obtained by dissolving iron in dilute sulphuric acid :—

$$Fe + SO_2(OH)_2 = SO_2 \cdot O_2Fe + H_2,$$

or, as a bye-product in making sulphuretted hydrogen, when ferrous sulphide is dissolved in the same acid :—

$$FeS + SO_2(OH)_2 = SO_2 \cdot O_2Fe + H_2S.$$

It is also produced by gently roasting iron pyrites in the air, when a portion of the sulphur burns to sulphurous acid, and another portion is oxidized to sulphuric acid, which unites with the iron to form ferrous sulphate. Some varieties of pyrites—*e.g.* marcasite —are oxidized at the ordinary temperature when moistened with water and exposed to the air, and the decomposed mass yields a green solution of ferrous sulphate when treated with water.

The salt separates from its solution in bluish green crystals with 7 molecules of water; it is easily soluble in water, especially hot. It readily loses 6 molecules of water when heated, but the seventh molecule, the water of constitution (p. 86), is only expelled at about

300°, with a partial decomposition of the salt. The anhydrous salt is white, *but it regains its green colour when treated with water.* If heated to redness, the anhydrous salt decomposes into ferric oxide and sulphurous and sulphuric anhydrides (p. 164).

Both solid ferrous sulphate and its solution are partly oxidized when exposed to the air, with the formation of basic ferric sulphate of a reddish colour; and when crystals of the substance which have been exposed to the air are dissolved in water, this insoluble basic salt remains undissolved :—

$$6SO_2{\cdot}O_2Fe'' + 3O + 3H_2O = (?)[2(SO_2)_3O_6Fe_2''' + 2Fe'''(OH)_3.]$$

Ferrous sulphate unites with the sulphates of the alkalies (potassium and ammonium), and forms double sulphates containing 6 molecules of water—*e.g.* $SO_2{\cdot}O_2Fe + SO_2(OK)_2 + 6aq.$, corresponding *to the magnesium compound (p. 415). These double* sulphates oxidize less readily than ferrous sulphate itself. The salt is an important article of commerce, and is employed for the preparation of ferric acetate (used in dyeing), to produce a black colour with galls (writing ink), a blue colour with potassium ferrocyanide (Prussian blue), and in the preparation of indigo solutions.

Ferrous Carbonate: $CO{\cdot}O_2Fe$.—This compound is found in nature as *spathic iron ore* or *siderite*, sometimes crystallized in rhombohedra which are isomorphous with calcite, but usually in compact amorphous masses. Mixed with clay it forms *clay ironstone*—one of the most important of the English ores of iron. The salt is obtained as a voluminous white precipitate on mixing a solution of ferrous sulphate with one of sodium carbonate. This white precipitate gradually absorbs oxygen from the air and changes colour, becoming first of a dirty green and then of a brown colour, *and is finally completely converted into ferric hydrate*, while carbonic acid is set free—no carbonate containing iron in the ferric state is known. If the moist precipitate is rubbed up with sugar, it is somewhat protected from the action of the air, and a brownish mass is obtained which is used in medicine under the name of *ferri carbonas saccharata.*

Like calcium carbonate and other carbonates, ferrous carbonate, though insoluble in pure water, dissolves in water containing carbonic acid. Mineral springs containing ferrous carbonate dissolved in carbonic acid are called *chalybeate* springs. The water has a bitter, inky taste, and when exposed to the air becomes turbid from

ferric hydrate. The dissolved ferrous carbonate is decomposed by the oxygen of the air into ferric hydrate and carbonic acid :—

$$2CO \cdot O_2Fe'' \ + \ O \ + \ 3H_2O = \ 2Fe'''(OH)_3 \ + \ 2CO_2.$$

Ferrous Phosphate: $\left.\begin{matrix} PO \\ PO \end{matrix}\right\} O_6Fe_3 + 8H_2O$, is found in nature as the mineral *vivianite*, sometimes crystalline, but usually as an earthy powder of a dull blue colour. The compound is precipitated when a solution of sodium phosphate is added to one of ferrous sulphate, and is used in medicine. It is at first white, but becomes blue or green by partial oxidation. By heating iron with phosphoric acid, a solution is obtained which after some time deposits colourless needles of the composition : (?) $PO\left\{\begin{matrix} O_2Fe \\ OH \end{matrix}\right. + H_2O$.

FERRIC COMPOUNDS.

Ferric Oxide : Fe_2O_3.—This compound occurs in immense quantities in the mineral kingdom, either in lustrous crystals belonging to the hexagonal system—*specular iron*—or more commonly in amorphous masses, with or without water, as the important iron ores included under the name of *hæmatite*. It may be obtained artificially in the crystalline state by strongly glowing a mixture of dry ferrous sulphate and common salt, or in the amorphous state by heating dry ferrous sulphate or ferric hydrate. The red amorphous powder obtained by either of the last-named methods is used for polishing and as a pigment, and is known as *colcothar*, *caput mortuum*, or *rouge*. A fine variety of rouge is obtained by glowing ferrous oxalate in the air. Ferric oxide is completely insoluble in water, and after heating to redness dissolves in acids with difficulty.

Ferric Hydrate : $Fe(OH)_3$ is thrown down as a red-brown flocculent precipitate when ammonia is added to a solution of a ferric salt. When washed with water and dried, it forms a brown amorphous mass, insoluble in water. Some important ores of iron, and the rust which forms when iron is exposed to the air, consist essentially of ferric hydrate

. Freshly precipitated ferric hydrate dissolves not only in acids, but also in a solution of ferric chloride, producing a dark red solution. If this solution of basic chloride is placed in a vessel of

which the bottom is closed with a piece of parchment paper and then floated on water, hydrochloric acid diffuses through, and there remains in the dialyser a solution of colloid ferric hydrate as a blood-red liquid (*dialysed iron*). The addition of a small quantity of sulphuric acid, or of an alkali or salt, at once causes the precipitation of the ferric hydrate from this solution as a gelatinous mass.

The use of ferric hydrate as an antidote in cases of poisoning by arsenic has been already referred to (p 236).

Like alumina, ferric oxide is a weak base, and its soluble salts can only be crystallized with difficulty. The normal salts are white or pale yellow when anhydrous, brown or yellow when hydrated ; the basic salts are yellow or red.

Ferric Sulphate: $(SO_2)_3O_6Fe_2$.—This salt is produced by oxidizing a solution of ferrous sulphate with nitric acid, with the addition of the one molecule of sulphuric acid for each two molecules of anhydrous ferrous sulphate:—

$$2SO_2 \cdot O_2Fe'' + SO_2(OH)_2 + O = (SO_2)_3O_6Fe_2''' + H_2O.$$

When the nitric acid is dropped into the hot solution of ferrous sulphate and sulphuric acid, the liquid first becomes dark brown and nearly black from the compound of ferrous sulphate with the nitric oxide produced by the reduction of the nitric acid (p. 194), until, when sufficient nitric acid has been added, the whole of the nitric oxide is evolved with effervescence, and the dark-red liquid now contains no ferrous sulphate. If no sulphuric acid is added to the ferrous sulphate, a larger quantity of nitric acid is required, and the solution then contains a mixture of ferric sulphate and ferric nitrate.

On evaporating the aqueous solution of the salt, ferric sulphate remains as a white amorphous powder, which attracts water from the air, and deliquesces to a dark red liquid, with a bitter astringent taste. An excess of ammonia when added to its aqueous solution precipitates ferric hydrate, but if less ammonia is added than is required to completely decompose it, a brown precipitate of a basic salt is produced. The oxidation of ferrous sulphate in the air produces a similar compound (p. 446).

A solution of ferric sulphate, when mixed with one of the potassium sulphates and the mixed solution allowed to evaporate slowly, deposits yellowish crystals of *potash-iron alum*. The corresponding ammonium compound *ammonia iron alum*: $\begin{matrix} SO_2 \\ SO_2 \end{matrix} \Big\} \begin{matrix} O_2Fe \\ ONH_4 \end{matrix}$ +

$12H_2O$, crystallizes more readily. The crystals are usually of a violet colour, possibly due to organic compounds contained in the ammonia.

Ferric Nitrate: $(NO_2)_3O_3Fe$, is prepared by dissolving iron in moderately concentrated nitric acid. From the red solution so obtained, the salt can only be crystallized with difficulty. The solid compound deliquesces in the air.

Ferric Phosphate (*Orthophosphate*): $(PO)O_3Fe$, is obtained as a yellow amorphous precipitate when ferric chloride is mixed with sodium phosphate. It is insoluble in water and acetic acid, but dissolves in strong inorganic acids.

Ferric Pyrophosphate closely resembles the preceding salt, and is insoluble both in water and acetic acid, but forms a soluble compound with sodium phosphate or pyrophosphate. The soluble double pyrophosphate is prepared by adding sodium pyrophosphate to the ferric salt until it is just dissolved; from this solution alcohol precipitates the double salt. Its aqueous solution is colourless, and does not possess the strong astringent taste of the other soluble ferric salts. It is used in medicine. (See Appendix.)

Ferric carbonate does not appear to exist. Ferric oxide is too weak a base to unite with carbonic acid. On adding a solution of sodium carbonate to one of ferric chloride, a brown precipitate of ferric hydrate is produced, and the carbonic acid which is set free partly unites with the excess of sodium carbonate to form the acid carbonate.

Triferric Tetroxide, *Magnetic Oxide of Iron*: $Fe_3O_4 = Fe''O, Fe_2''''O_3$.—This oxide is found in nature as black, well-developed, regular octahedra, especially in chlorite rocks. It further occurs as crystalline masses, and more largely in rough granular deposits. Magnetic oxide of iron, so called because pieces of it sometimes form natural magnets, is one of the most valuable ores of iron. Small lustrous octahedra of the oxide may be obtained artificially by heating bright iron wire to redness in a porcelain tube, and leading a current of steam over it. The water is then decomposed according to the equation:—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

Magnetic oxide of iron is soluble in hydrochloric acid, but the solution does not then contain a chloride corresponding to the oxide, but a mixture of ferric and ferrous chlorides. If ammonia is gradually added to this solution, a precipitate of ferric hydrate is first formed, and then one of ferrous hydrate. But if the solution is poured, with stirring, into an excess of ammonia, a dark-green precipitate is produced, which becomes black and granular when boiled. This is the hydrate of the magnetic oxide, and remains unchanged in the air. The same compound may also be obtained by converting two-thirds of a solution of ferrous chloride into ferric chloride by passing chlorine, then mixing this, when the excess of chlorine has been driven off, with the other third of the solution of ferrous chloride, and finally pouring the mixed solution into an excess of ammonia and boiling.

Ferric Acid.—The free acid, which would have the composition: $Fe^{vi}O_2(OH)_2$, has not yet been prepared; its potassium salt, *potassium ferrate*: $FeO_2(OK)_2$, is obtained by heating a mixture of reduced iron with twice its weight of potassium nitrate. The oxidation of the iron takes place with a considerable evolution of heat, and on extracting the cold mass with water the potassium ferrate dissolves with a red colour. On evaporating this solution in a vacuum, dark-red crystals are deposited. The salt may also be obtained by passing chlorine through concentrated cooled caustic potash containing freshly precipitated ferric hydrate in suspension:—

$$Fe(OH)_3 + 5KOH + 3Cl = FeO_2(OK)_2 + 3KCl + 4H_2O.$$

Iron forms two compounds with each of the halogens—chlorine, bromine, and iodine—corresponding to ferrous and ferric oxide respectively.

Ferrous Chloride: $FeCl_2$.—The anhydrous compound is obtained by heating iron wire in a stream of hydrochloric acid gas, when it sublimes at a high temperature in white, glistening iridescent crystals which feel soft and talc-like to the touch. It melts at a red-heat, and then solidifies to a crystalline mass. It is easily soluble in water, and on evaporating the aqueous solution without access of air, green crystals of the compound: $FeCl_2 + 4H_2O$ separate out. The same compound may be obtained by dissolving iron in hydrochloric acid and evaporating down. A solution of ferrous chloride, when exposed to the air, is gradually oxidized to basic ferric chloride.

Ferric Chloride : Fe_2Cl_6.—Although ferrous chloride readily unites with a further quantity of chlorine, an atom of iron can never decompose more than two molecules of hydrochloric acid. And when iron is dissolved in the acid, ferrous chloride is always produced, never ferric chloride. Anhydrous ferric chloride may be obtained by heating iron in dry chlorine, and then sublimes in nearly black, lustrous, crystalline plates. It is far more volatile, and therefore sublimes much more easily than ferrous chloride. When exposed to the air it becomes yellow, and deliquesces, forming a yellow or reddish solution ; it is also soluble in alcohol and ether, and is even abstracted from its aqueous solution when shaken with ether. The aqueous solution, which is also obtained by dissolving iron in aqua regia, or by passing chlorine through a solution of ferrous chloride, deposits reddish, deliquescent crystals of the compound : $Fe_2Cl_6 + 12H_2O$, when evaporated to a syrup. This compound, when heated, decomposes into water and hydrochloric acid, which pass off with some anhydrous ferric chloride, while ferric oxide remains behind. An aqueous solution of ferric chloride dissolves freshly precipitated ferric hydrate in considerable quantities, producing a dark-red liquid, from which ferric hydrate is again precipitated on diluting with water and heating.

Ferric chloride unites with the chlorides of potassium and ammonium to form double salts, which are deposited in bright-red crystals of the composition : $Fe_2Cl_6 + 4KCl + 2H_2O$ and $Fe_2Cl_6 + 4NH_4Cl + 2H_2O$, when the mixed solutions are evaporated down.

The *bromides* of iron closely resemble the chlorides.

Ferrous Iodide : FeI_2.—This compound is obtained by heating iron filings with iodine in a porcelain crucible. A small quantity of iodine is first added, then an excess, and the heating continued as long as vapours of iodine are evolved. The salt then remains as a grey crystalline mass, easily soluble in water. An aqueous solution of ferrous iodide may also be obtained by digesting iron filings with water and iodine—the iron being in excess. On evaporating this solution, crystals of the composition : $FeI_2 + 4H_2O$, are deposited. This solution dissolves more iodine when digested with it, and the dark-red solution so produced probably contains ferric iodide : Fe_2I_6, which has not yet been obtained in the solid form.

The compounds of iron with sulphur do not exactly correspond

with its oxides. A sesquisulphide (see Appendix): Fe_2S_3, and corresponding to ferric oxide, is not yet known for certain. On the other hand, the sulphide most widely distributed in nature is the disulphide: FeS_2, to which no corresponding oxide is known.

Ferrous Sulphide: FeS, is prepared as a black crystalline mass, by heating three parts of iron filings with nearly two parts of flowers of sulphur. If an excess of sulphur is employed, no compound richer in sulphur is obtained, but the excess is volatilized. Iron and sulphur unite together even at ordinary temperatures if the finely powdered mixture is moistened with water. When large quantities are used the heat of combination is often sufficient to violently expel a portion of the mixture from the vessel in which the reaction takes place.

Ferrous sulphide is insoluble in water, but is decomposed by acids. With hydrochloric or dilute sulphuric acid it yields sulphuretted hydrogen, and is therefore largely used to prepare this gas.

Ferric Disulphide: FeS_2.—This compound is widely distributed in the mineral kingdom, occurring either in bright yellow crystalline masses, or in well-developed lustrous cubes or other forms belonging to the regular system. In these forms it is known as *iron-pyrites*. It may also be prepared in the form of a yellow powder by gently heating powdered ferrous sulphide with about its own weight of sulphur, until the excess of this latter substance is expelled. Iron-pyrites is so hard that it strikes sparks with steel; unlike ferrous sulphide, it is not attacked by dilute acids, and is not therefore adapted for the preparation of sulphuretted hydrogen. When heated strongly it parts with some of its sulphur, leaving compounds of ferrous sulphide with more or less sulphur, according to the degree and duration of the heating. If iron-pyrites is heated in the air, a large portion of the sulphur is oxidized to sulphurous anhydride, and for this reason immense quantities of pyrites are employed in the manufacture of sulphuric acid. Many kinds of iron-pyrites contain small quantities of copper-pyrites, and traces of the noble metals, and the residues of these pyrites after roasting are often worked for copper and other metals.

Besides iron-pyrites, which crystallizes in the regular system, a second modification of ferric disulphide is known, the crystals of which belong to the rhombic system, and which is distinguished

from iron-pyrites by the readiness and rapidity with which it oxidizes when exposed to moist air—evolving at the same time a considerable amount of heat. This variety of pyrites is called *marcasite*; and the chief product of its oxidation is ferrous sulphate, which is obtained in considerable quantities from it.

A third sulphide of iron is also found in nature, which contains less sulphur than iron-pyrites, and not unfrequently has the composition: Fe_7S_8, or, if considered as a compound of ferrous sulphide and iron-pyrites: $6FeS,FeS_2$. This bronze-coloured mineral is known as *magnetic pyrites*, because it is attracted by the magnet. It crystallizes in the hexagonal system.

COMPOUNDS OF IRON AND CYANOGEN.

Although the compounds of iron with cyanogen corresponding to ferrous and ferric chlorides have not yet been prepared pure, the double salts which ferrous and ferric cyanide yield with the cyanides of other metals are among the best known and most stable of chemical compounds. Various views are held as to the chemical constitution of these substances, but in the present state of our knowledge it is perhaps best to write their formulæ empirically, without entering into the question of their constitution. The best known of these, and that from which all the others are prepared, is

Potassium Ferrocyanide: $K_4Fe''Cy_6 + 3H_2O = 4KCy, Fe''Cy_2 + 3H_2O$.—This compound, known in trade as *yellow prussiate of potash*, or simply as *yellow prussiate*, crystallizes from its aqueous solution in large, pale-yellow, quadratic plates, which are soft, and therefore difficult to powder. Heated to 100° or a little above, it loses its water of crystallization, and then becomes white and brittle, so that it can be easily pulverized. It is soluble in water, but insoluble in alcohol; 100 parts of water dissolve 25 parts at the ordinary temperature and 50 parts at the boiling-point.

Potassium ferrocyanide is obtained from potassium cyanide—a salt which is extremely poisonous, and which is readily decomposed by dilute acids. From this it might be expected that the ferrocyanide would also be poisonous, but experiment has proved that considerable quantities may be taken internally without any injurious or even unpleasant effects. When taken into the system it

soon gets into the blood, and in a short time can be detected in the urine, in which it is expelled unchanged from the body.

The salt is readily obtained from potassium cyanide by digesting an aqueous solution with iron filings or powdered ferrous sulphide. In the former case, caustic potash and hydrogen are also produced; in the latter potassium sulphide:—

$$6KCy + Fe + 2H_2O = K_4FeCy_6 + 2KOH + H_2$$

and

$$6KCy + FeS = K_4FeCy_6 + K_2S.$$

The same process goes on in the manufacture of potassium ferrocyanide on a large scale, except that instead of using potassium cyanide itself materials are employed which, when heated with potassium carbonate, produce this substance. For this purpose, organic compounds rich in nitrogen, such as blood, horn, hair, leather, are mixed with potash and iron filings, and fused at a red heat. During the process the carbon and nitrogen of the organic substances unite with the potassium and form potassium cyanide; and when the fused mass is afterwards extracted with water this substance acts upon the iron, which has been partly converted into ferrous sulphide by the sulphur of the crude materials, in the manner explained above. The salt which separates out on evaporation is purified by recrystallization; it often contains potassium sulphate.

Potassium ferrocyanide is not acted upon by carbonic acid nor even by dilute acids, and the potassium cyanide in combination with the ferrous cyanide has, therefore, acquired new properties, and has become more stable. The iron, too, has lost many of the properties which are possessed by the ferrous salts; ammonia does not precipitate ferrous hydrate, nor does ammonium sulphide throw down ferrous sulphide. And that potassium ferrocyanide is not an ordinary double salt of 4 molecules of potassium cyanide and 1 molecule of ferrous cyanide is proved by the fact that it is not decomposed by dilute acids like other true double cyanides. The double cyanide of nickel and potassium: $2KCy,NiCy_2$, a compound soluble in water, at once gives a precipitate of nickel cyanide with dilute hydrochloric acid, while the potassium cyanide is decomposed into potassium chloride and hydrocyanic acid. But no ferrous cyanide is separated by hydrochloric acid from the apparently analogous compound potassium ferrocyanide.

Many attempts have been made to explain this peculiar behaviour of potassium ferrocyanides and other similar compounds, but as yet without success. That potassium ferrocyanide when heated with dilute sulphuric acid leaves a compound containing 1 molecule of ferrous cyanide and 1 molecule of potassium cyanide, seems to prove that one of the four molecules of potassium cyanide in the ferrocyanide is more firmly combined than the other three.

An aqueous solution of potassium ferrocyanide is decomposed by strong acids (hydrochloric or sulphuric acid), with the formation of hydroferrocyanic acid : H_4FeCy_6, and the potassium salt of the acid employed. If finely powdered potassium ferrocyanide is *heated* with dilute sulphuric acid, hydrocyanic acid is evolved (p. 313), and there remains potassium sulphate with the compound we have just mentioned : $KCy,FeCy_2$. This is a white substance, turning blue in the air. Potassium ferrocyanide, when powdered and heated with moderately concentrated sulphuric acid, undergoes a further decomposition. There are produced ferrous, potassium, and ammonium sulphates with the evolution of a gas which consists chiefly of carbonic oxide. But since traces of other gases are mixed with the carbonic oxide, this method is not suitable for preparing the pure substance.

When heated in an iron crucible, potassium ferrocyanide is decomposed into iron carbide and potassium cyanide (p. 359). Fused with manganese peroxide or red-lead, potassium cyanate and ferric oxide are produced (p. 361). And when mixed with potassium carbonate and sulphur and fused, potassium sulphocyanate results (p. 361). If chlorine is led through a solution of potassium ferrocyanide, the iron is oxidized to the ferric state and some of the potassium converted into chloride, producing a compound called potassium ferricyanide : $K_3Fe'''Cy_6 = 3KCy,Fe'''Cy_3$ (p. 457).

Potassium ferrocyanide, like all other soluble ferrocyanides, is distinguished by its reactions with ferric chloride and soluble copper salts. When highly diluted it gives with the former a dark blue precipitate of Prussian blue, and with the latter a chocolate brown precipitate of copper ferrocyanide. With a soluble lead salt a solution of potassium ferrocyanide gives a white precipitate of the corresponding lead salt. The following equations represent these reactions :—

$$3K_4Fe''Cy_6 + 2Fe_2'''Cl_6 = 12KCl + Fe_4'''Fe_3''Cy_{18}.$$
Prussian blue

$$K_4FeCy_6 + 2CuCl_2 = 4KCl + Cu_2FeCy_6.$$
Copper ferrocyanide

$$K_4FeCy_6 + 2(NO_2)_2O_2Pb = 4NO_2 \cdot OK + Pb_2FeCy_6.$$
Lead ferrocyanide

The majority of the ferrocyanides are insoluble in water; those of the alkalies and alkaline earths are soluble, but that of barium only with difficulty.

Sodium Ferrocyanide: $Na_4FeCy_6 + 12H_2O$.—This salt corresponds closely to the potassium compound, except that it contains considerably more water of crystallization. It may be obtained by boiling Prussian blue with caustic soda, ferric hydrate and soluble sodium ferrocyanide being produced :—

$$Fe_4'''Fe_3''Cy_{18} + 12NaOH = 4Fe(OH)_3 + 3Na_4FeCy_6.$$

Other soluble ferrocyanides may be obtained in similar ways.

Ammonium Ferrocyanide: $(NH_4)_4FeCy_6 + 3H_2O$, crystallizes in bright yellow quadratic prisms, and is isomorphous with the potassium salt.

Prussian Blue: $Fe_4'''Fe_3''Cy_{18} = 4Fe'''Cy_3, 3Fe''Cy_2$.

Various dark blue compounds are known under the name of Prussian blue, but the commonest insoluble compound has the above composition; it is obtained on adding potassium ferrocyanide to a solution of ferric chloride or some other ferric salt. The compound may be considered as consisting of three molecules of potassium ferrocyanide in which the twelve atoms of potassium have been displaced by four of triad iron. This compound may be best obtained by adding potassium ferrocyanide to excess of a boiling solution of ferric chloride or nitrate. The commercial product generally contains some soluble Prussian blue (see below).

Prussian blue can only be washed on the filter with difficulty; when dry it forms a deep blue, hygroscopic powder, which under pressure assumes a lustre like copper. It is insoluble in water and dilute mineral acids, but dissolves in strong hydrochloric acid.

When warmed with concentrated acids it is decomposed. Oxalic acid dissolves the compound to a deep blue liquid, which is used as a blue ink. Alkalies and alkaline carbonates and even the alkalies of soap decompose it, separating ferric hydrate and reproducing potassium ferrocyanide :—

$$\left.\begin{matrix}Fe\\K\end{matrix}\right\}Cy_4,FeCy_2 \quad + \quad 3KOH \quad = \quad K_4FeCy_6 \quad + \quad Fe(OH)_3.$$

Prussian blue cannot, therefore, be used for dyeing or printing articles which are to be washed with soap.

A variety of Prussian blue, $KFe'''Fe''Cy_6$, soluble in pure water to a deep blue solution, is obtained when ferric chloride is added to a large excess of potassium ferrocyanide, and is known as *soluble Prussian Blue.*

Hydroferrocyanic Acid : H_4FeCy_6.—This acid is obtained in small white crystalline plates when a concentrated solution of potassium ferrocyanide free from air is mixed with strong hydrochloric acid in the cold :—

$$K_4FeCy_6 \quad + \quad 4HCl \quad = \quad 4KCl \quad + \quad H_4FeCy_6.$$

The crystals separate more readily if a little ether is added. They are afterwards brought upon a filter and washed with water containing ether. The compound is soluble in alcohol and in water, but is insoluble in hydrochloric acid and ether. It behaves like a tetrabasic acid, and when mixed with potassium carbonate again produces potassium ferrocyanide. It is rapidly oxidized in the air and becomes of a blue colour.

Potassium Ferricyanide : $K_3Fe'''Cy_6 = 3KCy,Fe'''Cy_3$.—This compound, which is known in trade as *red prussiate*, differs from the ferrocyanide by containing its iron in the ferric state. It is produced by abstracting potassium from the ferrocyanide, when the cyanogen thus set free unites with the iron and changes it from the ferrous to the ferric state. This is best done by leading chlorine into a solution of potassium ferrocyanide until a portion of the liquid no longer gives a blue precipitate with ferric chloride :—

$$K_4Fe''Cy_6 \quad + \quad Cl \quad = \quad KCl \quad + \quad K_3Fe'''Cy_6.$$

The salt separates out on evaporating its aqueous solution in dark-red, lustrous, rhombic prisms, easily soluble in water and insoluble in alcohol. Its aqueous solution is of a dirty green colour and decomposes on standing, especially when exposed to sunlight, depositing a blue precipitate. The readiness with which it again forms potassium ferrocyanide, especially in the presence of alkalies, makes it a powerful oxidizing agent.

Potassium ferricyanide gives no blue precipitate with ferric salts, but only a brown colour, but with ferrous salts it gives a fine blue precipitate, closely resembling Prussian blue, and called —

Turnbull's Blue : $Fe_3''Fe_2'''Cy_{12} = 3Fe''Cy_2,2Fe'''Cy_3$.—The precipitate is formed according to the equation :—

$$2K_3FeCy_6 + 3FeCl_2 = 6KCl + Fe_3''Fe_2'''Cy_{12}.$$

The compound, like Prussian blue, is decomposed by caustic alkalies, reproducing potassium ferricyanide, while ferrous hydrate is precipitated. At the same time, and especially with excess of alkali, a portion of the ferrous hydrate is oxidized to ferric hydrate by the potassium ferricyanide, which is reduced to the ferrocyanide.

When a ferrous salt is added to an excess of potassium ferricyanide a blue precipitate is formed soluble in pure water. This has the formula $KFe''Fe'''Cy_6$, and appears to be identical with soluble Prussian blue. Both compounds yield insoluble Prussian blue when a ferric salt is added to their aqueous solutions.

Hydroferricyanic Acid: H_3FeCy_6.—This compound separates, like the corresponding hydroferrocyanic acid, on mixing a solution of potassium ferricyanide with strong hydrochloric acid in the cold. It forms brown crystals, which are easily decomposed.

Sodium Nitroprusside : $Na_2Fe'''Cy_5(NO) + 2H_2O$.—This salt, which contains one atom of sodium less than the ferricyanide, and one atom of cyanogen displaced by the monad radical : NO (nitryl), crystallizes more easily than the corresponding salt of potassium. It may be prepared in the following manner. Two parts of potassium ferrocyanide are gently warmed with 3 parts of strong nitric acid which has been diluted with an equal volume of water, until a portion of the liquid no longer gives a blue precipitate either with ferric chloride or with ferrous sulphate. The liquid is then allowed

to cool, so that potassium nitrate which has been produced shall crystallize out; the acid liquid is then poured off, diluted with water, and neutralized with sodium carbonate.

On evaporating this solution sodium nitroprusside crystallizes out on cooling in large, dark-red, transparent crystals, easily soluble in water and in dilute alcohol. The aqueous solution gradually decomposes, especially when exposed to light, and deposits a blue precipitate. Sodium nitroprusside does not precipitate ferric salts, but is especially characterized by the dark purple colour which it produces with alkaline sulphides, and even with sulphuretted hydrogen. The colour soon changes to a blue, and afterwards becomes a dirty brown. This reaction is so delicate that by its means the presence of the most minute traces of an alkaline sulphide or of a nitroprusside may be detected.

Detection of Iron Compounds.

The presence of small quantities of iron in any form may be recognized by the colour of the borax bead produced in the blowpipe flame. In the outer or oxidizing flame, the ferric oxide colours the bead reddish-yellow, the colour becoming fainter on cooling. In the inner or reducing flame, the bead becomes of an olive-green colour, due to ferrous oxide. These colours cannot be observed in the presence of some other metals—*e.g.* cobalt—which obscure the colours produced by the oxides of iron.

An aqueous solution of a *ferrous* salt gives no precipitate with sulphuretted hydrogen, but a black precipitate of ferrous sulphide with ammonium sulphide. Caustic soda or ammonia precipitates ferrous hydrate from the same solution; the precipitate is first white, but soon oxidizes and becomes green and then brown. Potassium ferrocyanide gives a white precipitate rapidly oxidizing to Prussian blue, while potassium ferricyanide gives a blue precipitate (Turnbull's blue) at once.

When a stream of sulphuretted hydrogen is led through a solution of a *ferric* salt, a white precipitate of sulphur falls down, and the ferric salt is reduced to the ferrous state:—

$$Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S.$$

Similarly, the black precipitate which ammonium sulphide produces in ferric salts is a mixture of ferrous sulphide and sulphur. Caustic soda or ammonia, when added to a solution of a ferric salt, pre-

cipitates brown ferric hydrate; the presence of potassium tartrate prevents the precipitation.

If a ferric salt containing phosphoric acid is precipitated with ammonia, the precipitate is not ferric hydrate, but ferric phosphate. Potassium ferrocyanide when added to a ferric salt gives a dark-blue precipitate of Prussian blue. Potassium ferricyanide produces no precipitate, but only a brown colour.

Iron, in the form of a ferric salt, may be separated from the metals of the alkaline earths by precipitating with ammonium chloride and ammonia. Ammonium sulphide precipitates iron in any form, but does not throw down the alkaline earths.

Iron is separated from aluminium by digesting with an excess of caustic soda, which dissolves aluminium hydrate, but not ferric hydrate.

MANGANESE.

Chemical Symbol: Mn.—*Atomic Weight*: 55.

Manganese is closely related to iron in its properties, and has nearly the same atomic weight. Its compounds are also usually found associated with iron in nature. The most important minerals containing manganese are its oxygen compounds, and of these ***pyrolusite*** (manganese peroxide: MnO_2) is found in by far the largest quantities. Other manganese minerals are ***braunite*** (manganic oxide: Mn_2O_3), ***manganite*** (manganic hydrate: $\left\{\begin{matrix} MnO \cdot OH \\ MnO \cdot OH \end{matrix}\right)$, ***hausmannite*** (trimanganic tetroxide: Mn_3O_4), ***manganese-spar*** (manganous carbonate: $CO \cdot O_2Mn$), ***psilomelane*** and ***wad*** (impure manganic perhydrate). Manganese also occurs in nature as its silicate, and in combination with sulphur as various sulphides.

The metal itself is of but little interest. It may be obtained by heating a mixture of precipitated manganous carbonate and oil to redness, and then again heating this mixture with charcoal powder and anhydrous borax to the highest temperature of a wind furnace. The metal so obtained, which contains carbon and other impurities (see App.), is of a grey colour with a reddish tinge, very hard and brittle, and with a high melting-point. It has a specific gravity of about 7·2, and oxidizes when exposed to moist air. The metal

dissolves easily in dilute sulphuric, hydrochloric, or even nitric acid, producing the corresponding manganous salts.

Manganese unites with oxygen in no less than five proportions, forming oxides of very different chemical properties, and in which the manganese plays the part of a diad triad, tetrad, hexad, and heptad element. These compounds are the following :—

Manganous oxide : MnO . . .	Strong base
Manganic oxide : Mn_2O_3 . . .	Very weak base
Manganese peroxide : MnO_2 . .	Indifferent
Manganic acid : H_2MnO_4 . . .	Dibasic acid
Permanganic acid : $HMnO_4$ . .	Monobasic acid.

Of these oxides, manganous oxide corresponds to ferrous oxide, manganic oxide to ferric oxide, and an intermediate compound of these two : Mn_3O_4, to the magnetic oxide of iron. An oxide of iron corresponding to manganese peroxide is unknown, but we are acquainted with the corresponding sulphide in iron-pyrites. Finally, manganic acid corresponds to ferric acid, but no compound of iron is known similar to permanganic acid.

Manganous Oxide : MnO.—This oxide remains as a greenish powder when manganous carbonate is ignited out of contact with air, or in a stream of hydrogen. It may also be obtained by heating a mixture of manganous chloride and sodium carbonate. Manganous oxide is a strong base, and dissolves easily in hydrochloric, sulphuric, or nitric acid. When heated in the air it absorbs oxygen and is converted into trimanganic tetroxide : Mn_3O_4. Unlike the iron compound, it is not reduced to the metallic state by hydrogen, even at a high temperature.

Manganous Hydrate : $Mn(OH)_2$, is deposited as a white precipitate when caustic soda is added to a solution of a manganous salt. It rapidly darkens, especially when exposed to the air, and finally becomes completely converted into dark brown manganic hydrate.

Ammonia produces the same precipitate, but the precipitation is prevented by the presence of ammonium salts, since manganous hydrate forms soluble compounds with these.

The most important of the *manganous compounds—i.e.* those in which the metal is a diad—are the following :—

Manganous Sulphate : $SO_2 \cdot O_2Mn + 7H_2O$.—This salt is pro-

duced, with evolution of oxygen, when manganese peroxide is heated with strong sulphuric acid :—

$$MnO_2 + SO_2(OH)_2 = SO_2{\cdot}O_2Mn + H_2O + O.$$

The filtered solution, when sufficiently concentrated and freed from iron, deposits, below 6°, the salt in clear, rose-coloured, tabular crystals. At the ordinary temperature the salt crystallizes with only five molecules of water, and at higher temperatures other hydrated salts may be obtained. Like magnesium and ferrous sulphates, the salt unites with the alkaline sulphates, forming double sulphates with six molecules of water.

Manganous Nitrate : $(NO_2)_2{\cdot}O_2Mn + 6H_2O$. If manganous carbonate is dissolved in nitric acid and the solution evaporated down, manganous nitrate is obtained, and the salt is not oxidized as in the case of iron. It yields pink crystals, which are highly deliquescent, and are hence obtained only with difficulty ; when dried and heated it darkens in colour, and manganese peroxide separates out.

Manganous Carbonate : $CO{\cdot}O_2Mn$, is thrown down as a white precipitate when sodium carbonate is added to a solution of a manganous salt. It remains unchanged in the air when moist, and only slightly darkens when dried. The salt is therefore much more stable than ferrous carbonate. Manganous carbonate occurs in nature as the mineral *manganese-spar*, crystallizing in rose-red rhombohedra, isomorphous with spathic iron ore and calcite.

Manganous Chloride : $MnCl_2 + 4H_2O$.—Of the two chlorides of iron, ferric chloride is the more stable, and ferrous chloride readily combines with chlorine. But manganous chloride is by far the most stable chloride of the metal. The compound is produced when manganous carbonate is dissolved in hydrochloric acid, and is also a bye-product in the preparation of chlorine from manganese peroxide. As already stated (p. 98), manganese tetrachloride : $MnCl_4$, is first produced, but is so unstable that it at once breaks up into manganous chloride and free chlorine. But as the manganese peroxide used for the preparation of chlorine always contains iron, the manganous chloride produced when it is dissolved in hydrochloric acid always contains ferric chloride. Various methods are used to separate the iron, one of which consists in heating the dried residue in a Hessian crucible to low redness : the ferric chloride is then partly volatilized and partly

converted into insoluble basic chloride, but the manganous chloride remains unchanged. The mass is afterwards powdered and extracted with hot water; and on evaporating the violet-coloured solution, manganous chloride with four molecules of water separates out in pink-coloured crystals. It is very easily soluble in water, and deliquesces in moist air; when heated, it parts with all its water, accompanied by a trace of hydrochloric acid. Manganous chloride unites with ammonium chloride and forms a crystalline double salt of the composition: $MnCl_2,2NH_4Cl + H_2O$.

Manganous Sulphide: MnS, is found in the mineral kingdom as *alabandite*, in black cubes, or in crystalline masses. It is obtained artificially as a flesh-coloured precipitate by mixing a solution of a manganous salt with one of sodium sulphide. It easily dissolves in dilute acids with evolution of sulphuretted hydrogen. —*Manganese Disulphide*: MnS_2, has not been prepared artificially, but occurs in nature as the mineral *hauerite* in reddish-brown crystals belonging to the regular system.

Manganic Oxide: Mn_2O_3, occurs in nature as the mineral *braunite* in black lustrous crystals belonging to the quadratic system.

Manganic Hydrate: $\left\{\begin{matrix} MnO\cdot OH \\ MnO\cdot OH \end{matrix}\right.$ is found also in nature as *manganite* in dark-brown rhombic prisms or crystalline masses. It is prepared as a dark-brown amorphous precipitate when a solution of manganous chloride is mixed with ammonium chloride and ammonia and exposed to the air. Unlike manganous hydrate, it is insoluble in ammonium chloride.

Manganic oxide is a weak base, and combines with acids with difficulty. Its salts decompose easily, especially when warmed, and are converted into manganous compounds.

Manganic Sulphate: $(SO_2)_3O_6Mn_2{}'''$, may be obtained as a dark-green amorphous powder by digesting pure manganic hydrate with concentrated sulphuric acid. It deliquesces when exposed to the air, forming a red liquid, and is a difficult compound to prepare. Somewhat more stable is its double compound with potassium sulphate, *manganese alum*: $\begin{matrix} SO_2 \\ SO_2 \end{matrix}\Big\}\begin{matrix} O_3Mn \\ OK \end{matrix} + 12H_2O$, which is obtained by mixing the solution of the two sulphates.

Manganic Chloride is a very unstable compound, and unknown in the solid state. When manganic hydrate is treated with hydrochloric acid in the cold a dark brown liquid is obtained, which probably contains manganic chloride, but which continually evolves chlorine.

Trimanganic Tetroxide : $Mn_3O_4 = MnO,Mn_2O_3$, is found in nature as the mineral *hausmannite* in brown quadratic crystals. It is the most stable oxide of manganese, and may be heated to redness in the air without change. If manganese peroxide is strongly heated as long as oxygen is evolved, this compound remains as a reddish powder, and when manganous oxide or carbonate is heated in the air it absorbs oxygen and produces the same substance. Hydrochloric acid dissolves trimanganic tetroxide, forming manganous chloride, while chlorine is evolved.

Manganese Peroxide: MnO_2, is the commonest and most important of the manganese minerals, and as such is known by the name *pyrolusite*. It crystallizes in grey rhombic prisms, with a metallic lustre, but is usually found in rough masses often fibrous in structure. The chief European localities where it is found are Thuringia and on the Lahn in Germany, in Bohemia, in France, and in Spain. Manganese peroxide gives a *grey* streak on paper or porcelain, and may thus be distinguished from other manganese minerals. which give a brown streak. The compound may be artificially prepared by carefully heating manganous carbonate with potassium chlorate and extraction with water, or by heating manganous nitrate or the hydrated peroxide.

Manganese peroxide is an indifferent substance, insoluble in water and in nitric acid, even when concentrated. Strong sulphuric acid dissolves it with formation of manganous sulphate and free oxygen ; hydrochloric acid converts it into manganous chloride and chlorine. Substances which are easily oxidized, such as sugar, oxalic acid, &c., reduce manganese peroxide in the presence of sulphuric acid. Oxalic acid is thus completely converted into carbonic acid and water, while the peroxide becomes manganous sulphate. A process based upon this reaction is used to determine the quantity of the peroxide contained in commercial pyrolusite. Every molecule of manganese peroxide oxidizes a molecule of oxalic acid to carbonic acid, and it is, therefore, only necessary to know the weight of the latter substance, which may be either

collected and weighed, or estimated from the loss in weight, in order to determine the value of any particular sample of the ore :

$$\begin{cases} CO\cdot OH \\ CO\cdot OH \end{cases} + MnO_2 + SO_2(OH)_2 = 2CO_2 + SO_2\cdot O_2Mn + 2H_2O.$$

Manganese peroxide is largely used for many technical purposes chiefly for the manufacture of chlorine and bleaching powder. When heated, it liberates considerable quantities of oxygen, and becomes converted into trimanganic tetroxide.

Manganese Perhydrate, of uncertain composition, is obtained as a dark-brown amorphous powder when a solution of manganous chloride is precipitated by sodium hypochlorite, or when chlorine is passed through a solution containing suspended manganous hydrate. The hydrate also separates when carbonic acid is passed through a solution of potassium manganate, which is then changed into potassium permanganate. The same change takes place if a very dilute solution of potassium manganate is boiled.

Manganic Acid : $MnO_2\begin{cases} OH \\ OH \end{cases}$—The anhydride : MnO_3, of this acid is obtained as a red deliquescent mass by dropping a solution of potassium permanganate in sulphuric acid upon dry sodium carbonate, and passing the vapours evolved through a tube surrounded by a freezing mixture. It is unstable even at the ordinary temperature, and is decomposed by water with separation of black oxide of manganese, and simultaneous formation of permanganic acid.

Potassium Manganate: $MnO_2\begin{cases} OK \\ OK \end{cases}$—This salt is obtained by the oxidation of any oxide of manganese in the presence of free alkali—for example, when any compound of manganese is fused with a mixture of potassium (or sodium) carbonate, and a little nitre. It may be obtained purer by the following process. Five parts of powdered caustic potash are mixed with a little water and 4 parts of powdered manganese peroxide stirred up with it ; this mixture is next heated nearly to boiling, and 3½ parts of powdered potassium chlorate added. After evaporating the mass to dryness, it is heated in a crucible to low redness for one and a half hours, and the cold mass extracted with a little *cold* water. The intensely green solution of potassium manganate so obtained deposits dark green, almost black, rhombic crystals of the salt when evaporated in a vacuum over sulphuric acid. The reaction is represented by the following equation :—

$$3MnO_2 + 6KOH + ClO_2\cdot OK = 3MnO_2(OK)_2 + KCl + 3H_2O.$$

Potassium manganate is an unstable compound; its aqueous solution changes on standing, especially when warmed, and becomes red from formation of potassium permanganate—hence the name *chameleon mineral* sometimes given to the salt.

Permanganic Acid: $MnO_3 \cdot OH$.—This monobasic acid is only known in solution, and is so unstable that it rapidly decomposes. On the other hand, the anhydride —*permanganic anhydride*: $Mn_2O_7 = \left.\begin{matrix} MnO_3 \\ MnO_3 \end{matrix}\right\} O$, may be obtained by adding potassium permanganate in small quantities at a time to well-cooled strong sulphuric acid. *It then separates from the olive-green solution of permanganic acid as drops of a heavy red oil*, which soon decompose with evolution of oxygen.

Potassium Permanganate: $MnO_3 \cdot OK$.—This compound, the best known of the permanganates, is obtained by boiling the green solution of potassium manganate, or better, by leading a stream of carbonic acid through it. In the former case there are produced potassium permanganate, manganese perhydrate, and caustic potash; in the latter case, potassium carbonate is formed instead of the hydrate:—

$$3MnO_2(OK)_2 + 2H_2O = 2MnO_3 \cdot OK + MnO_2 + 4KOH.$$
$$3MnO_2(OK)_2 + 2CO_2 = 2MnO_3 \cdot OK + MnO_2 + 2CO \cdot (OK)_2.$$

For the preparation of the salt a solution of potassium manganate is warmed and a stream of carbonic acid led through it until the solution has become of a bright red colour. The clear solution is then run off from the precipitate and evaporated down, when potassium permanganate separates on cooling in long, dark-red, almost black, needles, with a metallic lustre. *The salt is isomorphous with potassium perchlorate. It is tolerably easily* soluble in water; at the ordinary temperature it requires 16 parts, but much less quantities at the boiling-point.

Potassium permanganate is one of the most powerful oxidizing agents with which we are acquainted, and attacks a number of bodies which are not affected by other oxidizing substances. It liberates chlorine from hydrochloric acid, oxidizes oxalic acid to carbonic acid, ferrous salts to ferric salts, sulphurous acid to sulphuric acid, &c. If the oxidizing solution of potassium permanganate contains free sulphuric acid, manganous sulphate is formed, and five atoms of oxygen are set free from each two molecules of the permanganate for the purposes of oxidation; but if the solution is neutral, hydrated

manganese peroxide is produced, and only three molecules of oxygen are liberated from two molecules of the salt :—

$$2MnO_3\cdot OK + 3SO_2(OH)_2 = 2SO_2\cdot O_2Mn + SO_2(OK)_2 + 3H_2O + 5O.$$
$$2MnO_3\cdot OK + H_2O = 2MnO_2 + 2KOH + 3O.$$

If finely powdered potassium permanganate is dropped into concentrated sulphuric acid, a green solution is obtained, and oxygen accompanied by considerable quantities of ozone is evolved.

Owing to its powerful oxidizing properties, potassium permanganate cannot be filtered through paper ; the paper is at once turned brown, and a reduced solution of a green or brown colour runs through. The facility with which potassium permanganate oxidizes organic substances generally makes it well adapted for purposes of disinfection. A solution of the crude salt or of the sodium compound is largely used in England under the name of *Condy's fluid.*

The other permanganates resemble that of potassium ; they are all of a red colour and soluble in water.

Detection of Manganese Compounds.

The amethyst colour imparted by a small quantity of a manganese compound to a bead of borax in the oxidizing flame of the blowpipe, and the disappearance of this colour when the bead is brought into the reducing flame, serve to detect the metal even in the presence of iron. Still more delicate is the green colour due to a manganate produced when a minute quantity of any manganese compound is fused on a piece of platinum foil with sodium carbonate and a little potassium nitrate. The test may be confirmed by dissolving the green mass in water, acidulating and warming, when the solution becomes pink (permanganate). The flesh-coloured precipitate of manganous sulphide produced when ammonium sulphide is added to a solution of a manganous salt, and the darkening of the white precipitate (manganous hydrate) thrown down by ammonia on exposure to the air, are characteristic reactions of manganese compounds. But the colour of the sulphide is obscured by a small quantity of a salt of iron, which gives black ferrous sulphide with the ammonium sulphide.

Ferric salts are at once distinguished from those of manganese by the white precipitate of manganous ferrocyanide, produced when a solution of potassium ferrocyanide is added to one of a manganous salt. Iron and manganese, which so often occur

together, may be approximately separated by the addition of ammonium chloride and ammonia, which only precipitates ferric hydrate. The solution must be quickly filtered, otherwise manganic hydrate is produced by oxidation, and this is not dissolved by ammonium chloride. A more exact method consists in adding an excess of sodium acetate to the *dilute* solution of the two salts and then boiling, when the whole of the iron is precipitated as basic ferric acetate, while manganous acetate remains in solution.

CHROMIUM.

Chemical Symbol: Cr.—*Atomic Weight*: 52·2.

Chromium, so-called on account of the various and beautiful colours of its compounds (χρῶμα = colour), is not very widely distributed in nature, and never occurs in the metallic state. By far the most important mineral containing chromium, and that from which its compounds are always prepared, is *chrome-iron ore*: FeO,Cr_2O_3.

Metallic chromium is only of scientific interest, and has not yet been applied to any useful purpose. It may be obtained, according to Wöhler, by mixing one part of violet chromic chloride with two parts of a fused mixture of potassium and sodium chlorides, and heating this with two parts of granulated zinc in a Hessian crucible under a layer of potassium-sodium chloride. The crucible is heated up to the boiling-point of zinc, recognized by the bubbling noise, kept at this temperature for ten minutes, then removed from the furnace and knocked several times on the floor to cause the metal to unite at the bottom of the crucible. On breaking open the crucible when cold, a regulus of an alloy of zinc and chromium is obtained, which is treated with dilute nitric acid until all the zinc is dissolved. The chromium then remains as a pale grey, crystalline powder. According to Bunsen, chromium may be obtained by electrolyzing a concentrated solution of chromic chloride. It then forms brittle lustrous scales, of the colour of iron. The metal is not oxidized by moist air so rapidly as iron; its specific gravity is about 6·5. When heated in the air it becomes covered with a thin film of the oxide, imparting to it various colours, like steel; it is only slowly oxidized in dry air, even at a red-heat. Hydrochloric acid dissolves the metal with evolution of hydrogen;

sulphuric acid acts similarly on warming. Nitric acid, even when hot and concentrated, does not act on it.

Chromium, like manganese, forms several compounds with oxygen. We are acquainted with—*chromous oxide* : CrO, *chromic oxide* : Cr_2O_3, *chromium dioxide* : CrO_2, *chromic anhydride* : CrO_3, and *perchromic acid* : $HCrO_4$ (?). The oxide corresponding to the magnetic oxide of iron has also been described. Chromic oxide and chromic anhydride are the most important and best known of these compounds. The former, like alumina and other sesquioxides, is a weak base, while chromic anhydride possesses strong acid properties.

CHROMIC OXIDE AND CHROMIC SALTS.

Chromic Oxide : Cr_2O_3.—This compound, which is isomorphous with alumina and ferric oxide, is amorphous or crystalline according to its mode of preparation, but always possesses a green colour. Chromic oxide may be obtained by a variety of methods, of which the following are the most important :—

(i.) By heating chromic hydrate.

(ii.) By heating mercurous chromate to redness :—

$$2CrO_2\begin{cases}OHg\\OHg\end{cases} = Cr_2O_3 + 4Hg + 5O,$$

when it remains as a dark green powder.

(iii.) By igniting ammonium dichromate :—

$$O\begin{cases}CrO_2\cdot ONH_4\\CrO_2\cdot ONH_4\end{cases} = Cr_2O_3 + 4H_2O + N_2,$$

when the chromic oxide remains behind in olive green scales.

(iv.) By very strongly heating a mixture of common salt and potassium dichromate covered with a layer of common salt in a Hessian crucible. On extracting the fused mass with water, the chromic oxide remains as glistening iridescent crystals :—

$$O\begin{cases}CrO_2\cdot OK\\CrO_2\cdot OK\end{cases} = Cr_2O_3 + K_2O + 3O,$$

the common salt only serving to assist the crystallization of the chromic oxide.

(v.) Finally, by passing the vapour of chromyl chloride through a porcelain tube heated to redness :—

$$2CrO_2Cl_2 = Cr_2O_3 + 2Cl_2 + O,$$

when chlorine and oxygen are given off, and the chromic oxide is deposited on the walls of the tube in lustrous dark-green crystals, which are so dark in colour as to appear almost black. These crystals are as hard as corundum, and have a specific gravity of 5·2.

Strongly ignited chromic oxide is insoluble in acids, even in concentrated sulphuric acid. It may be heated either in the air or in hydrogen to the highest temperatures of our furnaces without change; but is reduced when strongly heated with charcoal. When heated with potassium (or sodium) carbonate and exposed to the air, or with the addition of a little nitre, chromic oxide gives soluble potassium (or sodium) chromate. Insoluble compounds containing chromium—*e.g.* chrome-iron ore—are thus brought into solution.

Chromic oxide easily dissolves in molten glass as well as in borax, and the chromic silicate or borate so produced possesses a beautiful green colour. On account of this property and because it remains unchanged at a high temperature, chromic oxide is largely used for colouring glass green and for painting on porcelain.

Chromic oxide, like alumina and other sesquioxides, is a weak base. It unites with acids and with bases, forming, in the latter case, compounds which correspond to the aluminates. These compounds, sometimes called *chromites*, include chrome-iron ore: $FeO,Cr_2O_3 = \left.\begin{matrix}CrO\\CrO\end{matrix}\right\} O_2 Fe''$, referred to above, and which is distinguished by the difficulty with which it is attacked by most acids. Among other chromites are the soluble green compounds produced by digesting freshly precipitated chromic hydrate with caustic potash or soda. These compounds are, however, less stable than the corresponding aluminates, and are decomposed on boiling their solutions. It is remarkable that chromic hydrate when mixed with ferric hydrate is not dissolved by caustic alkalies.

Chromic Hydrates of the formula: $Cr_2O_3xH_2O$ separate when a solution of a chromic salt is mixed with ammonia as a bluish-green bulky precipitate, which when dried forms a dirty-green powder. Heated to about 220°, its constitution is represented by $Cr_2O_3H_2O$. Heated more strongly it begins to glow throughout its entire mass at one particular temperature, and is then converted into dark-green chromic oxide, which is now insoluble in acids. Freshly precipitated

chromic hydrate easily dissolves in acids, and produces two kinds of differently coloured chromic salts ; the solutions of the one kind are green, and those of the other violet. The violet salts change into green by continued boiling, but on allowing the latter to stand for some time a change takes place from the green to the violet. The violet salts crystallize easily ; but the green solutions, when evaporated down, leave a green amorphous mass.[1] Chromic hydrate, precipitated by ammonia from a solution of a violet salt, is somewhat soluble in an excess of the reagent, but is rendered completely insoluble on boiling.

A hydrate of chromium of a fine green colour is known in trade as *Guignet's green*, and has the composition : $Cr_2O_3, 2H_2O = O\left\{\begin{matrix}Cr(OH)_2\\Cr(OH)_2\end{matrix}\right.$ It is obtained by fusing a mixture of potassium dichromate and crystallized boric acid, and then extracting the fused mass with water. During the reaction, potassium and chromic borates are produced, and the latter compound is decomposed when treated with water.

Chromic Sulphate : $(SO_2)_3O_6Cr_2 + 15H_2O$.—This salt crystallizes in violet octahedra, when chromic hydrate is dissolved in sulphuric acid and allowed to stand for some time. If its solution is mixed with potassium sulphate, the two sulphates unite to form *chrome-alum* : $\begin{matrix}SO_2\\SO_2\end{matrix}\left\}\begin{matrix}O_3Cr\\OK\end{matrix}\right. + 12H_2O$, which crystallizes out in fine dark-purple octahedra when the solution is allowed to evaporate slowly.

Chrome-alum is, however, best prepared by the reduction of a mixture of potassium dichromate and sulphuric acid by some easily oxidized substance, such as sulphurous acid or alcohol. The chromic acid which is thus set free by the sulphuric acid parts with oxygen, and is reduced to chromic oxide. One of the best reducing substances to employ is ordinary alcohol, which then becomes oxidized to the volatile compounds—aldehyde and acetic acid. To obtain chrome-alum in this way, 2 parts of a saturated solution of potassium dichromate are mixed with 3 parts of concentrated sulphuric acid in a large flask, and alcohol added drop by drop from a separating funnel, with continued agitation, until

[1] The chemical difference between the violet and green modifications is not definitely known. It is very probable, however, that the green varieties, at least in many cases, consist of basic salts.—ED.

the red liquid has changed to a dark green. On allowing the green liquid to stand for some time in an open dish it gradually becomes of a violet colour, and, in consequence of evaporation, small octahedra of chrome-alum begin to be deposited. If these small crystals are allowed to lie in the solution, which is kept in a cellar where the temperature is nearly uniform, and are turned daily, they gradually grow to large regular octahedra. The above reaction takes place according to the following equation :—

$$O\begin{cases}CrO_2\cdot OK\\ CrO_2\cdot OK\end{cases} + 4SO_2(OH)_2 = 2\begin{matrix}SO_2\\ SO_2\end{matrix}\begin{Bmatrix}O_2Cr\\ OK\end{Bmatrix} + 4H_2O + 3O,$$

in which the oxidation of the alcohol by the three atoms of oxygen is not shown.

As in ordinary alum, the potassium in chrome-alum may be displaced by any of the alkali-metals, or by thallium, without changing its crystalline form.

Chromic Nitrate : $(NO_2)_3O_3Cr + 9H_2O$, crystallizes with difficulty from the violet solution obtained by dissolving chromic hydrate in nitric acid.

Chromic Phosphate : $PO\cdot O_3Cr + 6H_2O$, falls as a dirty-green precipitate when a solution of sodium phosphate is added to one of chrome-alum. It becomes crystalline on standing under the liquid.

Chromic Chloride : Cr_2Cl_6.—This chloride sublimes in beautiful peach-blossom coloured scales, when a mixture of chromic oxide and charcoal is heated in a stream of dry chlorine ; it is distinguished from the corresponding chlorides of aluminium and iron by its insolubility in water. When heated in the air it loses chlorine, and takes up oxygen, being first converted into an oxychloride and then into chromic oxide.

A simple method of preparing considerable quantities is as follows. The dried mixture of chromic oxide, charcoal, and starch paste is placed in a Hessian crucible, on which is cemented a second crucible of similar size placed upside down, and through the bottom of which a hole is bored to receive the glass tube bringing the chlorine. The two crucibles are placed in a charcoal furnace so that the lower one is surrounded by the glowing charcoal, and is heated to redness, while the upper one is only moderately heated. Chlorine is then led into the upper crucible through a glass tube which fits the opening loosely, and

the lower crucible is raised to a bright red-heat. The carbonic oxide and the excess of chlorine escape through the opening at the top, and the chromic chloride condenses on the sides of the upper and cooler crucible; a portion of the chloride remains in the lower crucible loosely attached to the carbonaceous residue, from which it may be easily removed when cold.

Chromic chloride when pure is quite insoluble in water, but dissolves at once to form a green liquid when the water contains a *trace* of crystalline chromous chloride. Mere contact with the chromous chloride suffices to convert the insoluble violet chromic chloride into the soluble green variety.

By dissolving chromic hydrate in hydrochloric acid and evaporating down, a green hydrated chromic chloride is obtained, which loses water and hydrochloric acid when heated, and leaves a basic chromic chloride behind.

Chromous Chloride: $CrCl_2$.—If chromic chloride is heated to low redness in a stream of hydrogen it loses chlorine, and is converted into a white crystalline mass of chromous chloride. This chloride dissolves in water to a blue liquid, which then absorbs oxygen when exposed to the air, and produces an oxychloride. Chromous chloride, like ferrous chloride, can dissolve considerable quantities of nitric oxide, forming a dark-brown solution. The merest trace of this chloride can convert considerable quantities of the violet chromic chloride into the soluble green modification (see above).

When caustic potash is added to a solution of chromous chloride, a brown precipitate is produced, which is probably of *chromous hydrate*: $Cr(OH)_2$, but which possesses so strong an attraction for oxygen, that it decomposes water and forms *trichromic tetroxide*: Cr_3O_4, *with evolution of hydrogen.*

CHROMIC ACID AND THE CHROMATES.

Chromic Anhydride: CrO_3.

True chromic acid is unknown in the free state; when separated from its salts it breaks up into water and chromic anhydride. (See Appendix.)

Chromic anhydride, commonly known as chromic acid, is easily obtained by adding 1½ volume of concentrated sulphuric acid to 1 volume of a saturated solution of potassium dichromate at 50°. The mixture becomes strongly heated, and deposits on cooling long bright red prisms of the chromic acid liberated by the sulphuric acid. When quite cold the mother-liquor, containing acid potassium sulphate, is poured off, and the crystals dried first on an asbestos filter, and then by placing them on a porous plate of unglazed porcelain, which absorbs the remaining traces of water. By recrystallizing from a small quantity of water and repeating the drying process, the crystals may be obtained pure and free from sulphuric acid.

Chromic acid is easily soluble in water and deliquesces in moist air. The solution is of a reddish-brown or yellow colour according to its strength, and reacts strongly acid. Chromic acid contains one-half of its oxygen very loosely combined, and is decomposed into chromic oxide and oxygen not only when heated alone ($2CrO_3 = Cr_2O_3 + 3O$), but also when heated with sulphuric acid, chromic sulphate being formed in this case. In the same way it evolves chlorine with strong hydrochloric acid:—

$$2CrO_3 + 12HCl = Cr_2Cl_6 + 6H_2O + 3Cl_2$$ [1]

It oxidizes organic substances so powerfully that few can withstand its action. If the solution is filtered through paper, or if the crystals are dried with paper, the chromic acid at once becomes of a green colour from chromic oxide. Alcohol when dropped on the crystalline substance is so rapidly oxidized that it catches fire.

If a solution of chromic acid is mixed with hydrogen peroxide a compound of a beautiful blue colour is formed, which easily dissolves in ether. It has been suggested that this compound is *perchromic acid*, corresponding to permanganic acid, but its composition is doubtful (p. 91).

The Chromates.

The hypothetical chromic acid: $CrO_2\begin{cases}OH\\OH\end{cases}$ is, like sulphuric acid, a dibasic acid, but is distinguished from this and all other

[1] An excellent method of obtaining a long-continued, regular stream of chlorine consists in gently heating potassium dichromate with an excess of hydrochloric acid.—ED.

dibasic acids by the fact that it never produces acid salts. That acid salts of chromic acid might be produced cannot be doubted, but we are as yet unacquainted with the conditions under which they can exist. They decompose as soon as produced into the normal salts of dichromic acid : $O\left\{\begin{matrix} CrO_2 \cdot OH \\ CrO_2 \cdot OH \end{matrix}\right.$ and water. If, for example, normal potassium chromate : $CrO_2\left\{\begin{matrix} OK \\ OK \end{matrix}\right.$ is mixed with a solution of chromic acid, or with a stronger acid, then it is probable that acid potassium chromate is first produced :—

$$CrO_2\left\{\begin{matrix} OK \\ OK \end{matrix}\right. + CrO_2\left\{\begin{matrix} OH \\ OH \end{matrix}\right. = 2CrO_2\left\{\begin{matrix} OH \\ OK \end{matrix}\right.$$

or

$$CrO_2\left\{\begin{matrix} OK \\ OK \end{matrix}\right. + SO_2\left\{\begin{matrix} OH \\ OH \end{matrix}\right. = CrO_2\left\{\begin{matrix} OH \\ OK \end{matrix}\right. + SO_2\left\{\begin{matrix} OH \\ OK \end{matrix}\right.$$

and that two molecules of the acid chromate immediately afterwards break up into the normal dichromate and water :—

$$2CrO_2\left\{\begin{matrix} OH \\ OK \end{matrix}\right. = O\left\{\begin{matrix} CrO_2 \cdot OK \\ CrO_2 \cdot OK \end{matrix}\right. + H_2O.$$

These soluble dichromates are again converted into the normal chromates on the addition of a base :—

$$O\left\{\begin{matrix} CrO_2 \cdot OK \\ CrO_2 \cdot OK \end{matrix}\right. + 2KOH = 2CrO_2\left\{\begin{matrix} OK \\ OK \end{matrix}\right. + H_2O.$$

Similar relations to that between chromic acid and dichromic acid also exist between sulphuric and disulphuric acids (p. 167), and between phosphoric and pyrophosphoric acids (p. 219) ; the only difference being that the normal salts of disulphuric and pyrophosphoric acids are produced from the acid sulphates and acid phosphates respectively at a high temperature, while the change from the acid chromates to the normal dichromates takes place at the ordinary temperature. It is possible that acid chromates may exist at a low temperature.

Potassium Dichromate : $K_2Cr_2O_7 = O\left\{\begin{matrix} CrO_2 \cdot OK \\ CrO_2 \cdot OK \end{matrix}\right.$—This salt is manufactured on a large scale from chrome-iron ore : FeO, Cr_2O_3, and is the starting-point for the preparation of all other chromium compounds. It is obtained when the finely powdered ore is mixed with potassium carbonate and nitre and fused for some time. The iron is then oxidized to ferric oxide and the chromium

to chromic acid, which unites with the potassium and forms yellow potassium chromate. The latter compound goes into solution on digesting the fused mass with water. On the large scale the mixture of the pulverized ore and potassium carbonate, without nitre, is heated in a reverberatory furnace and the oxidation effected by excess of air. A certain quantity of lime is usually added, which keeps the mass porous and prevents complete fusion. The yellow solution of potassium chromate obtained by afterwards extracting with water (see App.) is then acidulated with sulphuric acid, which both destroys any excess of potassium carbonate and converts the normal chromate into red potassium dichromate, and the solution is allowed to crystallize. The chromate is converted into the dichromate because the latter salt crystallizes much more easily from its solutions, and can, therefore, be more readily purified.

Potassium dichromate, purified by recrystallization, forms orange-red tabular crystals of the above composition, and without water of crystallization. It dissolves in ten parts of water at the ordinary temperature, but is more soluble in hot water; the solution reacts faintly acid. When heated to low redness it melts unchanged to a dark red liquid, and at very high temperatures is decomposed. Concentrated sulphuric acid separates crystalline chromic acid from its aqueous solution. Sulphuretted hydrogen reduces a solution of potassium dichromate and produces a precipitate of chromic hydrate and sulphur, while the potassium is converted into sulphide or sulphydrate, which remains in solution:—

$$O\begin{cases}CrO_2\cdot OK\\CrO_2\cdot OK\end{cases} + 4H_2S = 2\,Cr(OH)_3 + 3S + K_2S + H_2O.$$

No precipitate of chromic hydrate is produced if hydrochloric or sulphuric acid is previously mixed with the solution of potassium dichromate; the red colour of the solution then changes to a green from the chromic chloride or sulphate produced.

If a solution of potassium dichromate is mixed with caustic potash or potassium carbonate until the red colour has become a pure yellow, and the solution evaporated down,

Potassium Chromate: $CrO_2(OK)_2$, separates out in yellow crystals, isomorphous with potassium sulphate. The salt is very easily soluble in water, and cannot therefore be so easily crystallized as the dichromate. Its yellow solution reacts slightly alkaline, and becomes red on the addition of an acid owing to the

formation of potassium dichromate, which in its other properties it closely resembles.

Sodium Chromate.—Both sodium chromate and dichromate closely resemble the corresponding potassium salts, except that they are much more soluble in water, and even deliquesce in the air.

Ammonium Dichromate: $O\begin{cases} CrO_2 \cdot ONH_4 \\ CrO_2 \cdot ONH_4 \end{cases}$ crystallizes in red scales, and otherwise resembles the potassium salt. It is easily soluble in water, and gives green chromic oxide when heated (p. 469).

Ammonium Chromate: $CrO_2(ONH_4)_2$, crystallizes in yellow needles on evaporating a mixture of aqueous chromic acid and excess of ammonia. The crystals remain unchanged in the air.

Calcium and *Strontium Chromates* crystallize in yellow prisms, and are much less soluble in water than the potassium salt. *Barium Chromate*: $CrO_2 \cdot O_2Ba$, is nearly insoluble in water, and separates as a pale-yellow precipitate when a solution of potassium chromate or dichromate is added to one of barium chloride. It is used as a yellow pigment.

The chromates of the heavy metals are coloured substances, insoluble in water.

Chlorochromic Acid and Chromyl Chloride.

Chromic acid, which resembles sulphuric acid in so many points, also forms a compound, chromyl chloride: $CrO_2\begin{cases} Cl \\ Cl \end{cases}$ corresponding to sulphuryl chloride: $SO_2\begin{cases} Cl \\ Cl \end{cases}$ in which the two atoms of hydroxyl of the hypothetical acid are displaced by chlorine. A second compound, corresponding to chlorsulphonic acid: $SO_2\begin{cases} Cl \\ OH \end{cases}$, and in which only one atom of hydroxyl is displaced, is known in the salts of chlorochromic acid—*e.g. potassium chlorochromate*: $CrO_2\begin{cases} Cl \\ OK \end{cases}$. The acid itself has not yet been prepared. To obtain this potassium salt, 3 parts of finely powdered potassium dichromate are mixed with water to a paste, then gently warmed with 4 parts of concentrated hydrochloric acid until a faint odour of

chlorine is perceptible. The salt afterwards separates in large red, tabular crystals as the clear, red solution cools :—

$$O\left\{\begin{matrix}CrO_2\cdot OK\\CrO_2\cdot OK\end{matrix}\right. + 2HCl = 2CrO_2\left\{\begin{matrix}Cl\\OK\end{matrix}\right. + H_2O.$$

The salt is decomposed by water, but dissolves in hydrochloric acid unchanged. When gently heated it evolves chlorine copiously.

Chromyl Chloride: $CrO_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$ is a blood-red, heavy liquid of 1·9 specific gravity, and boiling at 116°. It possesses a powerful piercing odour, and fumes in the air. In order to prepare this compound, 10 parts of common salt are fused together with 12 parts of potassium dichromate, the fused mass poured on to a clean iron plate and broken into pieces when cold. It is then introduced into a large retort connected with a condenser, and 40 parts of concentrated sulphuric acid, containing some Nordhausen acid, added. A brisk reaction ensues, which must afterwards be supported by a gentle heat, and the compound distils over into the well-cooled receiver. It is purified by repeated distillation, finally in a stream of carbonic acid gas. The reaction is represented by the following equation :—

$$O\left\{\begin{matrix}CrO_2\cdot OK\\CrO_2\cdot OK\end{matrix}\right. + 4NaCl + 6SO_2\left\{\begin{matrix}OH\\OH\end{matrix}\right. = 2CrO_2Cl_2 +$$
$$2SO_2\left\{\begin{matrix}OK\\OH\end{matrix}\right. + 4SO_2\left\{\begin{matrix}ONa\\OH\end{matrix}\right. + 3H_2O,$$

according to which 1 molecule of potassium dichromate and 4 molecules of sodium chloride give, when heated with an excess of sulphuric acid (about 9 molecules), 2 molecules of chromyl chloride, 2 of acid potassium sulphate, 4 of acid sodium sulphate, and 3 of water, for the retention of which at least 3 molecules of sulphuric acid are required.

Chromyl chloride is decomposed by water into chromic and hydrochloric acids. It acts energetically on phosphorus, sulphur, and many organic substances with the production of light and heat. When its vapour is led through a red-hot tube it is decomposed into chlorine, oxygen, and chromic oxide. If the requisite quantity of chromyl chloride is dropped into a solution of normal potassium chromate, containing a little acetic acid, the liquid becomes filled with crystals of potassium chlorchromate :—

$$CrO_2Cl_2 + CrO_2(OK)_2 = 2CrO_2\left\{\begin{matrix}Cl\\OK\end{matrix}\right.$$

Detection of Chromium Compounds.

Compounds of chromium, in any form, may be readily and certainly detected by simple blowpipe tests. When heated with sodium carbonate and a little nitre on a piece of platinum foil, they all produce yellow sodium chromate, and the fused mass, when dissolved in water and acidulated with acetic acid, gives a yellow precipitate of lead chromate on the addition of a few drops of a solution of lead acetate.

A trace of a chromium compound imparts a green colour to a borax bead (due to chromium borate), both in the oxidizing and reducing flame, but which becomes converted into yellow sodium chromate when heated for a long time in the oxidizing flame.

An aqueous solution of a chromate is recognized by the yellow precipitate of lead chromate produced on the addition of a solution of lead acetate; and by the change of the yellow or red solution to a green salt of chromic oxide when acted upon by sulphuretted hydrogen, sulphurous acid, alcohol, or other reducing agents in the presence of hydrochloric or sulphuric acid.

The soluble salts of chromic oxide all yield chromic hydrate with ammonium sulphide, ammonia, or caustic soda, and are not precipitated by sulphuretted hydrogen. In this respect the salts of chromic oxide resemble those of alumina. Freshly precipitated chromium hydrate, like aluminium hydrate, is easily dissolved by caustic soda, but the hydrate is reprecipitated on boiling, or when allowed to stand.

Compounds of chromic oxide may therefore be separated from those of alumina by adding excess of caustic soda and boiling; they may be separated from salts of iron by fusing with sodium carbonate and nitre, when the iron is converted into insoluble ferric oxide, while the chromium takes the form of a soluble chromate, which may be extracted by digesting the fused mass with water.

URANIUM.

Chemical Symbol: U.—*Atomic Weight*: 240.

This somewhat rare element is never found free in nature; it occurs almost exclusively as the oxide: $U_3O_8 = UO_2,2UO_3$, in the mineral *pitchblende*. The metal may be obtained by fusing

uranous chloride with sodium, best in an iron crucible, and then forms either a black powder or a hard metallic button of a grey colour. It melts at a red heat, and has a specific gravity of 18·7. The metal does not decompose water even at 100°, but oxidizes when heated in the air, and is easily dissolved by dilute acids.

Uranium unites with oxygen to form *uranous oxide*: UO_2, and *uranic oxide*: UO_3. A third (see Appendix) oxide also exists of the composition: U_3O_8, which may be considered as a compound of the first two: $UO_2 + 2UO_3$. Pitchblende consists chiefly of this oxide, but contains also compounds of lead, copper, arsenic, iron, manganese, cobalt, and other metals. To obtain pure uranium compounds from this mixture the following process may be adopted. The powdered mineral is heated with moderately concentrated sulphuric acid and small quantities of nitric acid added from time to time. When only a white insoluble residue (of lead sulphate, &c.) remains, the liquid is evaporated down to expel most of the acid, then diluted with water and the clear solution saturated with sulphuretted hydrogen to precipitate lead, copper, arsenic, &c. The solution is next filtered off from these sulphides, the iron oxidized again by nitric acid, and ammonia added in excess. The dark-yellow precipitate so obtained, which chiefly consists of ferric hydrate and ammonium uranate, is then well washed and treated with a warm concentrated solution of ammonium carbonate containing free ammonia, until all the uranium is dissolved and the precipitate consists entirely of dark-brown ferric hydrate. The yellow solution, which must be quickly filtered, deposits small, hard, yellow crystals of ammonium-uranic carbonate, and a further deposit of the same salt is obtained as a yellow powder when the solution is boiled. This compound when heated to redness leaves the pure dark-green oxide: U_3O_8.

Uranic Nitrate: $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\} O_2(UO_2) + 6H_2O$, is obtained in large yellow deliquescent prisms when the preceding or any other oxide of uranium is dissolved in nitric acid and the solution evaporated down. If the salt is heated to 250° until nitrous fumes are no longer evolved, it becomes changed into

Uranic Oxide: $UO_3 = (UO_2)O$, which remains behind as a yellow powder, and which when strongly heated loses oxygen and reproduces uranoso-uranic oxide: U_3O_8.

Uranic Sulphate: $SO_2 \cdot O_2(UO_2) + 3H_2O$, may be obtained by

decomposing the nitrate with sulphuric acid, and crystallizes in pale yellowish-green needles.

Uranic Carbonate.—Ammonium carbonate, when added to a solution of a uranium compound, produces a yellow precipitate, which, however, is not uranium carbonate, but a double carbonate of ammonium. This salt is soluble in an excess of ammonium carbonate, and if this solution is allowed to evaporate in the air, or if gently warmed, it deposits small yellow glistening crystals of the compound: $CO{\cdot}O_2(UO_2) + 2CO{\cdot}(ONH_4)_2$, which is only slightly soluble in water. This double salt is used to separate uranium from other metals.

Uranic Phosphate: $\left.\begin{matrix}PO\\PO\end{matrix}\right\} O_6(UO_2)_3 + PO\left\{\begin{matrix}O_2(UO_2)\\OH\end{matrix}\right. + H_2O$ is formed as a yellow, crystalline precipitate on adding a solution of phosphoric acid or a phosphate to one of uranic acetate. It is insoluble in acetic acid. If the solution of uranium contains ammonium chloride, the precipitate which is produced on the addition of a phosphate has the composition: $PO\left\{\begin{matrix}O_2(UO_2)\\ONH_4\end{matrix}\right.$ This compound is also insoluble in acetic acid, and is used to estimate phosphoric acid, especially in manures.

The mineral *autunite* is a double phosphate of uranium and calcium.

From the composition of the uranium compounds given above, it is clear that uranic oxide is not a triacid base like alumina, ferric oxide, and chromic oxide, but that it always combines only with two molecules of a monobasic acid, like lime, magnesia, and the oxides of other diad metals. Two atoms of oxygen are firmly united with an atom of uranium to form a diad radical: UO_2, called *uranyl*, and the salts of the oxide—*e.g.* uranic nitrate, are properly called uranyl salts—*e.g.* uranyl nitrate. This rule, however, is not followed, because no compound of the composition: $(NO_2)_6O_6U$, is known. If, then, uranic oxide: UO_3, is to be considered as uranyl oxide: $(UO_2)O$, we should expect that on dissolving this oxide in hydrochloric acid a chloride of the composition: $(UO_2)Cl_2$, would be obtained, according to the equation:—

$$(UO_2)O + 2HCl = (UO_2)Cl_2 + H_2O,$$

and as a matter of fact the compound: *Uranyl chloride*, which

crystallizes with difficulty from the yellow solution obtained by dissolving uranic oxide in hydrochloric acid, has this composition.

Uranic oxide unites with strong bases to form a series of compounds called *uranates*, in which it plays the part of an acid. All these salts, even those of the alkalies, are insoluble in water. *Potassium uranate*: $O\begin{cases}UO_2\cdot OK\\UO_2\cdot OK\end{cases}$ corresponding to potassium dichromate, is obtained as a yellow precipitate on adding caustic potash to a solution of uranium nitrate. It bears a high temperature without decomposition. *Sodium uranate* and *Ammonium uranate* closely resemble the potassium salt, and are obtained by adding caustic soda or ammonia to a solution of uranium nitrate. Ammonium uranate dissolves in ammonium carbonate in the cold, and when ignited in the air leaves uranoso-uranic oxide as a green powder.

Uranyl Sulphide: $(UO_2)S$, is precipitated as a black amorphous powder, nearly insoluble in water, when ammonium sulphide is added to a solution of an uranic salt. It is soluble in ammonium carbonate, and is therefore not thrown down if the solution to which the ammonium sulphide is added contains this salt.

Uranous Oxide: UO_2, which is produced by glowing uranic oxide or uranoso-uranic oxide in a stream of hydrogen, is a black or dark brown crystalline powder, insoluble in dilute hydrochloric acid, but dissolving in nitric acid and in concentrated sulphuric acid. If a solution of uranous oxide in sulphuric acid, which is of a green colour and contains *uranous sulphate*: $(SO_2)_2O_4U$, is mixed with caustic soda, a brown precipitate of uranous hydrate: $U(OH)_4$, is produced, which turns black on boiling.

Uranous Chloride: UCl_4, may be prepared by igniting a mixture of any oxide of uranium and charcoal in a stream of chlorine, and then sublimes in lustrous dark green octahedra. It is readily soluble in water and deliquesces in moist air.

Uranoso-uranic Oxide: $U_3O_8 = UO_2,2UO_3$, is obtained as a dark green powder, by glowing either uranous or uranic oxide in the air. In the former case oxygen is absorbed, in the latter it is given off. It is easily soluble in nitric acid, but only dissolves in

sulphuric or hydrochloric acid with difficulty, and withstands a high temperature without change.

Glass (or a borax bead) is coloured a bright green by this oxide, while uranic oxide imparts a greenish yellow tint, which fluoresces strongly in bright light.

COBALT AND NICKEL.

These twin metals (see Appendix) almost invariably occur in association with one another in nature, the one being in excess in some minerals, and the other in others. Both are constant constituents of metallic meteorites, though the nickel is always in excess. The two metals have nearly the same atomic weight, and their compounds are so much alike, chemically, that for a long time no method was known of separating them. Their salts are chiefly distinguished from one another by their colour: those of cobalt are red or blue, and those of nickel green.

The similarity between the two metals extends even to their names. The external appearance of the cobalt ores led to the belief that a valuable metal might be extracted from them by the ordinary metallurgical processes. But when all attempts in this direction proved futile, the German miners imagined the ores to be possessed of an evil spirit or *Kobold* (=sprite, goblin), and this word then gave the name cobalt to the metal afterwards discovered in the ores. In the same way, many attempts were made to extract copper from the commonest ore of nickel—Kupfer-nickel—which is itself of a copper colour; but when all these endeavours were in vain the ore was thrown on one side and called *Nickel* (an abusive word for an obstinate person in some South German dialects), a name which has now been retained for the metal itself.

Of the two metals, cobalt was first used in the arts, and in the form of its oxide, after it had been discovered that this compound dissolves in molten glass with a dark-blue colour, and that such glass when finely powdered yields a fine blue pigment (*smalt*). In the manufacture of smalt the nickel compounds are separated under the name of cobalt-speiss, and this was formerly thrown away as useless. At one time this speiss was used in Hesse for mending the roads, but when its value became known the road scrapings were carefully collected and worked for nickel.

Cobalt is only used technically in the form of its oxide, not as the metal; while nickel, on the other hand, is almost exclusively used in the metallic state for the preparation of alloys and for nickel-plating.

COBALT.

Chemical Symbol: Co.—*Atomic Weight*: 58·6.

Cobalt is only found native in metallic meteorites, and then in very small quantities. The most important minerals which contain the metal are *smaltite* or *speiss-cobalt*: $CoAs_2$, and *glance-cobalt*: $CoS_2,CoAs_2 = CoAsS$. From these ores, which usually contain copper, iron, and nickel, cobalt or a pure cobalt compound may be obtained by a variety of methods. To prepare cobalt from either of the above ores on the small scale, the following process may be adopted. The ore is first freed from some of its sulphur and arsenic by roasting in the air, then dissolved in hydrochloric acid, with the addition of small quantities of nitric acid, until completely decomposed. Sulphuretted hydrogen is next passed through the acid liquid to precipitate arsenic, copper, lead, &c., and after the iron has been again oxidized by nitric acid, a solution of sodium carbonate added until just neutral, by which all the iron is precipitated as ferric hydrate. The filtered solution, on further addition of sodium carbonate, gives a precipitate of the mixed carbonates of cobalt and nickel, which, when washed and digested with a strong solution of oxalic acid, are converted into the insoluble oxalates, both of which dissolve in strong ammonia. This solution of the oxalates in ammonia is then allowed to stand in the air for some time, so that the ammonia may slowly evaporate, when the whole of the nickel is precipitated as oxalate, while the cobalt remains in solution. The clear purple solution, which now only contains cobalt, is evaporated to dryness, the residue glowed, and then dissolved in hydrochloric acid, and after the excess of hydrochloric acid has been removed by heating, precipitated with a solution of oxalic acid. The cobalt oxalate: $\left\{\begin{matrix}CO\\CO\end{matrix}\right. O_2Co$, so obtained is decomposed when heated into carbonic acid and cobalt, the latter fusing at a sufficiently high temperature. To reduce the metal from the oxalate, a narrow,

deep, unglazed, porcelain crucible is filled with the dry salt, then covered, placed in a larger Hessian crucible lined with charcoal, and exposed to a high temperature in a wind furnace. The metal then melts to a steel-grey button, with a tinge of red. It has a specific gravity of 8·5, is malleable, and can be highly polished. It is only fused with difficulty, is more compact than iron, and is slightly magnetic. Cobalt is less readily oxidized than iron, but when heated in the air becomes covered with a film of the oxide; it dissolves in hydrochloric acid and dilute sulphuric acid, but less readily than iron, and then produces cobaltous chloride and sulphate respectively; nitric acid also dissolves it, forming cobaltous nitrate.

Cobalt unites in two proportions with oxygen, forming cobaltous oxide: CoO, and cobaltic oxide: Co_2O_3. The former is a strong base, while the latter possesses more the character of a peroxide.

Cobaltous Oxide: CoO; *Cobaltous Hydrate*: $Co(OH)_2$.

When caustic soda is added to a solution of cobaltous chloride, a lavender-coloured precipitate of a basic chloride is formed; the precipitate changes to pink cobaltous hydrate when boiled, but soon absorbs oxygen from the air, and becomes of a brownish colour. When this precipitate is heated out of contact with the air, it loses water and is converted into cobaltous oxide, forming a dull green powder. The same compound is produced when cobaltous carbonate is heated out of contact with air. When heated in the air, cobaltous oxide is converted into the three-quarter oxide—tricobaltic tetroxide: Co_3O_4, corresponding in composition to the magnetic oxide of iron. Cobaltous oxide dissolves in hydrochloric, sulphuric, or nitric acid, and produces bright red solutions.

Cobaltic Oxide: Co_2O_3; *Cobaltic Hydrate*: $Co(OH)_3$.

Cobaltic oxide is a black powder, insoluble in water, and is obtained by carefully heating cobaltous nitrate or cobaltic hydrate. The hydrate is produced when chlorine is led into an alkaline solution containing cobaltous hydrate in suspension. Such a solution is easily obtained by precipitating a cobaltous salt with excess of caustic soda. The reaction is as follows:—

$$Co(OH)_2 + NaOH + Cl = Co(OH)_3 + NaCl.$$

Cobaltic hydrate may also be obtained by precipitating a solution of a cobaltous salt with sodium hypochlorite, or a solution of bleaching powder. Like the oxide, it is also of a black colour, and

both compounds dissolve easily in hydrochloric acid. This solution appears at first to contain *cobaltic chloride*: $CoCl_3$, as but little chlorine is set free in the cold; if, however, the liquid is gently warmed, chlorine is liberated in abundance, and the solution now contains red cobaltous chloride.

Cobaltic oxide, when strongly heated in the air, loses oxygen and is converted into the oxide, Co_3O_4.

Cobaltous Sulphate: $SO_2{\cdot}O_2Co + 7H_2O$, is easily soluble in water, and separates from its aqueous solution in dark-red crystals, isomorphous with ferrous sulphate.

Cobaltous Nitrate: $(NO_2)_2O_2Co + 6H_2O$, crystallizes with difficulty in dark-red prisms, which deliquesce in the air. When heated it easily parts with oxygen and all its nitrogen as nitric peroxide, and leaves a residue of cobaltic oxide, which becomes cobaltoso-cobaltic oxide: Co_3O_4, when more strongly heated.

Cobaltous Nitrite is an unstable compound, and has not been prepared pure. If a neutral aqueous solution of a cobaltous salt is mixed with one of potassium nitrite in excess, a yellow, crystalline precipitate soon separates, which is a double nitrite of potassium and diad cobalt, and has the composition :—

$$(NO)_2O_2Co'' \quad + \quad 2NO{\cdot}OK \quad + \quad H_2O.$$

This compound is slightly soluble in cold water, and dissolves more readily when warm, forming a red solution.

A second double nitrite, but containing triad cobalt, is obtained when potassium nitrite is added in excess to a solution of a cobaltous salt strongly acidified with acetic acid. A double salt of the composition :—

$$(NO)_3O_3Co''' \quad + \quad 3NO{\cdot}OK,$$

with varying quantities of water, then separates also in the form of a yellow crystalline precipitate. This compound is only slightly soluble in water, but quite insoluble in water containing a small quantity of potassium nitrite or some other potassium salt. The corresponding nickel compound is easily soluble in water, and potassium nitrite is therefore used to separate cobalt and nickel.

Cobaltous Phosphate is thrown down as a bright-red precipitate, on adding a solution of sodium phosphate to a cobaltous salt.

Cobaltous Carbonate.—When sodium carbonate is mixed with

a cobaltous salt a pink precipitate is produced. This is not the normal carbonate, but a basic salt of varying composition.

Cobaltous Oxalate: $\left\{\begin{matrix}CO\\CO\end{matrix}\right.O_2Co$, is slightly soluble in water, and separates when oxalic acid is added to a cobaltous salt as a pink crystalline powder.

Cobaltous Chloride: $CoCl_2 + 6H_2O$, crystallizes on evaporating its aqueous solution in fine red prisms. When heated the salt loses water, and becomes of a blue colour. The same change is produced by concentrated hydrochloric acid. It forms a crystalline double salt with ammonium chloride of the composition: $CoCl_2 + NH_4Cl + 6H_2O$.

Cobaltic chloride, which in the free state is so unstable, unites with ammonia and forms a number of stable and most remarkable compounds, whose constitution still remains an unsolved problem. If an aqueous solution of cobaltous chloride is mixed with an excess of strong ammonia, the clear liquid exposed to the air until its brown colour has changed to a red, and then mixed with concentrated cold hydrochloric acid, a brick red crystalline powder of the composition:

$$CoCl_3,5NH_3 \quad + \quad H_2O,$$

and called *Roseocobaltic chloride*, separates out. The cobaltous chloride by standing in the air has become oxidized to a compound of triad cobalt. If the solution is precipitated with sulphuric acid, instead of with hydrochloric acid, a bright red crystalline precipitate of roseocobaltic sulphate is produced.

The dark red solution of roseocobaltic chloride becomes of a purple colour when *boiled*, and then deposits small, lustrous, purple crystals of *Purpureocobaltic chloride*: $CoCl_3,5NH_3$, on cooling. This compound differs only from roseocobaltic chloride by containing one molecule of water less.

With the formation of the purpureocobaltic chloride, a second compound called *Luteocobaltic chloride*: $CoCl_3,6NH_3$, is also produced, which is difficultly soluble in cold water, and is deposited when the hot solution cools as dark yellow crystals.

If the aqueous solutions of these chlorides are digested with silver oxide, silver chloride is produced, together with a strongly alkaline liquid, from which, however, the bases cannot be separated

as they decompose, with evolution of ammonia, when the solutions are concentrated. In what form the five or six molecules of ammonia exist in these compounds it is still uncertain. But the constitution of these compounds is possibly *not* that expressed by the above empirical formulæ, which represent them as double compounds of cobaltic chloride and ammonia.

Cobaltous Cyanide: $CoCy_2$.—If potassium cyanide is added to a cobaltous salt, a dirty-red precipitate of cobaltous cyanide is thrown down. This salt is insoluble in water, but readily dissolves in an excess of potassium cyanide, forming a double salt: $2KCy, CoCy_2$, which is decomposed by hydrochloric acid. If, however, the clear solution of this double salt is boiled with an excess of potassium cyanide, hydrogen is evolved, the cobalt oxidized, and

Potassium Cobalticyanide: $K_3Co'''Cy_6 = 3KCy,CoCy_3$, produced according to the equation:—

$$2KCy,Co''Cy_2 + 2KCy + H_2O = 3KCy,CoCy_3 + KOH + H.$$

On evaporating the solution the salt is deposited in yellow rhombic crystals of the above composition and without water. It is easily soluble in water, acids do not precipitate cobaltic cyanide, and it is generally similar to potassium ferricyanide, with which it is isomorphous. In the same way, the cobalt which it contains is neither precipitated with caustic soda nor with ammonium sulphide, but hydrochloric or sulphuric acid when added to its concentrated aqueous solution separates *hydrocobalticyanic acid*: H_3CoCy_6, which separates out as white needles on evaporation and addition of alcohol. In solutions of the salts of the heavy metals, potassium cobalticyanide produces insoluble precipitates of its various salts. The cupric compound, for example, is a pale-blue precipitate.

Cobalt unites with sulphur in several proportions, and produces the following compounds.

Cobaltous Sulphide: CoS, is obtained as a black amorphous precipitate when ammonium sulphide is added to a cobaltous salt, and is insoluble both in water and in dilute acids. The compound may also be obtained as a grey compact mass by heating a mixture of cobalt and sulphur.

Tricobaltic Tetrasulphide: $Co_3S_4 = CoS,Co_2S_3$, occurs in nature

in steel-grey octahedra of the regular system as the mineral *linnæite.*

Cobalt Disulphide: CoS_2, is not known in the free state, but only in combination with cobalt diarsenide as the mineral *glance-cobalt.*

Cobalt Diarsenide: $CoAs_2$, and *Cobalt Triarsenide*: $CoAs_3$, both occur in the mineral kingdom, the former as *speisscobalt* and the latter as *skutterudite.*

The chief application of cobalt in the arts is for the preparation of the stable blue pigment known as smalt.

Smalt is a potash glass which contains cobalt oxide instead of lime. It is prepared by fusing the partially roasted cobalt ores (*zaffre*) with quartz and potassium carbonate. The potassium silicate then unites with the cobalt silicate, producing a dark-blue glass. At the same time the compounds of sulphur and arsenic with the other metals (especially nickel) accompanying the cobalt collect at the base of the crucible, producing a speiss which is worked for nickel.

The blue cobalt glass is ground to an impalpable powder, and used in this form as a pigment. Various shades of blue are produced, depending chiefly on the amount of cobalt introduced into the glass, which seldom exceeds 7 or 8 per cent.

Smalt is one of the most beautiful of blue pigments, and is, at the same time, the most stable. It is not bleached in light, nor is it attacked by acids or alkalies. It is not, however, available for all purposes where a blue pigment is required, and since the introduction of so much cheap ultramarine the demand for the more expensive but more stable smalt has considerably diminished.

Detection of Cobalt Compounds.

The intense blue colour which traces of any cobalt compound impart to a bead of borax, in common with other kinds of glass, and the fact that the blue colour is permanent both in the reducing and in the oxidizing flame, makes it easy to detect these compounds. The salts may also be recognized by their red colour when hydrated and blue colour when anhydrous. Sulphuretted hydrogen produces no precipitate in acid solutions of cobalt salts, and in this way cobalt may be easily separated from copper, lead, and all those metals whose sulphides are precipitated from acid liquids by sulphuretted hydrogen. Cobaltous sulphide, like the

corresponding sulphide of nickel, after precipitation with ammonium sulphide, does not redissolve in dilute hydrochloric acid, and may thus be separated from the sulphides of iron, manganese and zinc, which are easily soluble in dilute acids.

NICKEL.

Chemical Symbol: Ni.—*Atomic Weight*: 58·6.

This metal, like cobalt, is only found native in metallic meteorites, but always in larger quantities than cobalt. The chief compound in which nickel occurs in nature is *Kupfernickel* or *niccolite*: NiAs, so called on account of its reddish colour. The metal is prepared from this and from cobalt speiss by removing the cobalt by a series of processes and then reducing with charcoal.

Metallic nickel was formerly almost exclusively brought into trade as small cubes, obtained by heating the compressed oxide in charcoal; it is now largely used in the form of rolled plates for the processes of nickel-plating. This commercial metal is far from pure, and usually contains copper and iron as well as arsenic and cobalt. A purer metal may be obtained by heating the carbonate or oxide in a stream of hydrogen, and then fusing the spongy mass so produced under borax at a high temperature. Large deposits of a hydrated double silicate of nickel and magnesium, and quite free from admixture with cobalt, have been more recently discovered in New Caledonia, and considerable quantities of the metal are now obtained from this source.

Nickel is a white metal with a yellowish tinge and a specific gravity of 8·6. It is malleable and ductile and, like cobalt, faintly magnetic. Nickel is very difficultly fusible, and only changes slightly in moist air; when heated in the air it becomes covered with a thin layer of oxide. Hydrochloric and dilute sulphuric acid dissolve the metal slowly, with evolution of hydrogen; nitric acid, when not too concentrated, converts it into the nitrate.

Just as the hydrated cobalt salts nearly all possess a red colour, the nickel salts are distinguished by their green colour. Nickel forms two oxides: nickelous and nickelic oxide, corresponding to the two oxides of cobalt.

Nickelous Oxide: NiO, is a dirty-green powder obtained by

heating its hydrate or carbonate. It dissolves in acids and forms green solutions.

Nickelous Hydrate: $Ni(OH)_2$, is thrown down as an apple-green precipitate when caustic soda is added to a nickel salt. It dries to a dark-green powder.

The same precipitate is produced by ammonia, but dissolves in excess of the reagent to a blue liquid.

Nickelic Oxide: Ni_2O_3, is a black powder produced on carefully heating nickel nitrate. The corresponding *hydrate* $Ni(OH_3)$ is obtained as a black amorphous powder when a salt of nickel is precipitated with sodium hypochlorite. Both nickelic oxide and hydrate dissolve in hydrochloric acid with evolution of chlorine and formation of nickel chloride; and both break up when heated into nickelous oxide and oxygen.

Nickel Sulphate: $SO_2 \cdot O_2Ni + 7H_2O$, crystallizes from its solutions in emerald-green prisms. Like other sulphates of the same composition, it forms double salts with the alkaline sulphates, of which the ammonium compound: $SO_2 \cdot O_2Ni + SO_2(ONH_4)_2 + 6H_2O$, is largely used in the arts for nickel-plating.

Nickel Nitrate: $(NO_2)_2O_2Ni + 6H_2O$, forms long green prisms, easily soluble in water, and deliquescing in the air.

Nickel Carbonate.—A basic carbonate is thrown down as a green precipitate when sodium carbonate is added to a nickel salt. The precipitate, like other insoluble nickel compounds, dissolves in ammonia or ammonium carbonate to a blue liquid.

Nickel Chloride: $NiCl_2 + 6H_2O$, is deposited from its aqueous solution when strongly concentrated as small green crystals, which, when heated, lose water and become yellow.

Nickel Cyanide: $NiCy_2$, is thrown down as a dirty green precipitate when a solution of potassium cyanide is carefully added to a salt of nickel. The salt is insoluble in water, but dissolves easily in an excess of potassium cyanide to form a double compound of the composition: $2KCy,NiCy_2 + H_2O$, which crystallizes in yellow prisms when the solution is evaporated down. Nickel cyanide produces similar double salts with the cyanides of sodium, barium, calcium, &c., from all of which it is again precipitated by hydrochloric acid. Potassium-nickel cyanide is not changed when boiled

with an excess of potassium cyanide ; no compound corresponding to potassium cobalticyanide is produced, nor does such a compound appear to exist. (See Appendix.)

Nickel Sulphide : NiS, is found in the mineral kingdom in fine hair-like crystals as the mineral ***millerite***. The same compound is produced as a black precipitate by adding sodium sulphide to a solution of a nickel salt. If precipitated with ammonium sulphide a portion of the precipitate dissolves and forms a dark brown solution.

Nickel Alloys.

The chief use of nickel in the arts is for the manufacture of various alloys, the most important of which is that known as *German-silver*, *argentan*, or *nickel-silver*, and which contains copper, zinc, and nickel in varying proportions. If the quantity of nickel is considerable the alloy has a white colour, with a faint yellowish tinge. German-silver is used for a variety of purposes, and forms the basis of the better kind of silver-plated ware. The five- and ten-pfennig pieces of the Germans, corresponding to our half-pence and pence, consist of an alloy of three parts of copper and one part of nickel. Alloys of nickel are also used for coinage purposes in Switzerland, Belgium, America, and Jamaica.

In recent years considerable quantities of nickel have been used for the process of nickel-plating, which consists in coating metallic articles with a thin layer of nickel by an electric current. The coating of nickel much improves the appearance, and at the same time only rusts slowly in the air. Nickel-plating is especially used for articles made of iron, which, when well deposited, it effectually protects from rust.

Detection of Nickel Compounds.

Nickel oxide dissolves in molten glass and borax, like cobalt oxide, but the colour is far less characteristic. In the oxidizing flame the borax bead is of a yellowish-brown colour, which becomes grey and opaque in the reducing flame from finely-divided metallic nickel.

A solution of a nickel compound is characterized by the black precipitate of nickel sulphide produced on the addition of ammonium sulphide, and especially that the precipitate is slightly soluble, forming a dirty-brown solution. In other respects nickel compounds closely resemble those of cobalt, except in their colour.

The salts of the two metals may be separated by the addition of acetic acid and potassium nitrite, when the cobalt is completely precipitated but the nickel remains in solution (p. 486). Salts of calcium, barium, and strontium must not be present, otherwise some of the nickel is precipitated with the cobalt.

ZINC.

Chemical Symbol: Zn.—*Atomic Weight*: 65·3.

Zinc is never found free in nature, but chiefly occurs in combination with carbonic acid as *smithsonite* or *calamine* (zinc carbonate: $CO \cdot O_2Zn$), and united with sulphur as *zinc blende* (zinc sulphide: ZnS). A further important ore of zinc is a silicate called *siliceous calamine* or *willemite*. Zinc is volatile at a bright red-heat, and its oxide cannot therefore be reduced, like iron and other metals, with charcoal in an ordinary furnace. All the zinc would then be volatilized and burnt. The zinc oxide, obtained by roasting any of the above ores in the air, is therefore heated with charcoal in specially constructed vessels of fireclay, resembling retorts, and in the cooler parts of which the volatilized zinc condenses.

Commercial zinc is never pure; even when freed from other less volatile metals by repeated distillation, it always contains more or less arsenic. This impurity may, however, be removed by stirring small quantities of nitre into the fused metal; a considerable quantity of the zinc is then oxidized together with the arsenic, which is converted into potassium arsenate. If all the arsenic has not been removed during the first operation, the process must be repeated. The presence of arsenic in zinc is best detected by the aid of Marsh's test (p. 239).

Zinc possesses very remarkable physical properties, which are not found in the same degree in any other metal. Under some circumstances it is tough and hard, under others soft and malleable, or it may be so brittle as to be easily powdered, and finally it is known as a gas. Zinc acquires these very various properties at different temperatures. The bluish-white metal, with a lamellar, crystalline fracture and a specific gravity of 7·15, is hard and tough at the ordinary temperature, and can neither be hammered nor rolled into plates; for this reason zinc was for a long time only

used for the preparation of brass and other alloys. The metal became, however, much more valuable when it was discovered that above the boiling-point of water—*i.e.* between 100° and 150°—it becomes soft and malleable, and can be hammered or rolled to thin plates. At a higher temperature, 200° and above, it is as brittle as antimony, and can be rubbed to powder in a hot mortar. Zinc melts at about 412°, and boils at a bright-red heat—*i.e.* about 1,000°.

Zinc, when heated in a crucible above its melting-point and then exposed to the air by opening the crucible, burns with a bluish-green flame, forming zinc oxide, which becomes distributed through the air of the room in light white flocks—the *lana philosophica* of the alchemists. The non-volatile zinc oxide which remains behind in the crucible has a fine yellow colour, but becomes white when cold.

Zinc oxidizes in moist air even more readily than iron, and becomes covered with a thin film of zinc oxide or basic zinc carbonate. But this film forms a compact layer over the metal, and so protects it from further oxidation that it scarcely increases in weight when exposed for a long time to the air. For this reason zinc is used for a variety of purposes for which iron, that rusts so easily and continuously, could not be employed. Large quantities of zinc are consumed in the process of galvanizing iron, which consists in coating iron plates or vessels with a layer of zinc, by immersing them in the molten metal. One of the most important and useful alloys—brass—contains a large proportion of zinc.

Zinc is easily dissolved by acids: hydrochloric and dilute sulphuric acid evolve hydrogen when acting on the metal; nitric acid produces nitric oxide, or if dilute, ammonia, and oxyammonia when sulphuric acid is also present (p. 188). Zinc, like iron, easily decomposes water at a low red heat. Since zinc oxide forms compounds with the alkalies which are soluble in water, the metal also dissolves in caustic alkalies, and in ammonia when warmed, and then liberates hydrogen.

Zinc only forms a single compound with oxygen, sulphur, or the halogens, respectively; it is a diad in all its compounds.

Zinc Oxide: ZnO.—This compound, the only oxide of zinc, is a soft white powder, infusible at a red heat. It is obtained by burning zinc in the air or by heating its hydrate, carbonate, or nitrate

When heated it becomes of a fine yellow colour, but is again white when cold.

Zinc oxide is used in medicine for some purposes, but is chiefly employed as a white pigment in the place of white-lead. This *zinc-white* does not cover so well as white-lead, but possesses the advantage of not blackening in the air. Sulphuretted hydrogen, which is contained in traces in the air of inhabited places, gradually converts both the zinc and lead compounds into sulphides, of which lead sulphide is black, but zinc sulphide is white, and is therefore not noticed.

Zinc Hydrate: $Zn(OH)_2$, is obtained as a gelatinous, white precipitate when a small quantity of caustic soda is added to a solution of a zinc compound. When washed and dried it remains as a white powder. The hydrate dissolves in excess of caustic soda and produces a soluble salt, *sodium zincate*, in which zinc oxide plays the part of an acid. It also dissolves in ammonia.

Zinc Sulphate, *white vitriol*: $SO_2 \cdot O_2Zn + 7H_2O$, is prepared by dissolving zinc or zinc oxide in dilute sulphuric acid, or on the large scale by gently roasting blende (zinc sulphide) and extracting with water. It crystallizes in large rhombic prisms, and when heated melts in its water of crystallization. This fused mass is sometimes cast into moulds, broken into pieces when cold, and so brought into the market for dyeing purposes. Zinc sulphate forms a basic sulphate when its solution is heated with zinc hydrate; it unites with alkaline sulphates to form crystalline double salts—*e.g.* $SO_2(OK)_2 + SO_2 \cdot O_2Zn + 6H_2O$.

Zinc Nitrate: $(NO_2)_2O_2Zn + 6H_2O$, crystallizes from its concentrated aqueous solution in four-sided prisms. It is very easily soluble in water and deliquesces in the air; when heated it melts in its water of crystallization.

Zinc Carbonate: $CO \cdot O_2Zn$, occurs in nature as the mineral *calamine* and occasionally in rhombohedra isomorphous with calcite, as *zinc-spar*. The precipitate obtained when sodium carbonate is added to a solution of a zinc salt is always a basic salt, or, in other words, a compound of zinc carbonate and hydrate.

Zinc Chloride: $ZnCl_2$.—This salt may be obtained either by heating zinc in chlorine, or by evaporating an aqueous solution and

distilling the residue. The distillate obtained by either of these processes is a white translucent mass. It eagerly attracts water from the air and deliquesces, and dissolves readily both in water and alcohol. Zinc chloride melts at 260° and does not appreciably volatilize at 400°; it is therefore often used instead of an oil-bath to heat substances to a high and constant temperature. Its boiling-point is about 700°.

An aqueous solution of zinc chloride is obtained by dissolving zinc in hydrochloric acid. If this solution is evaporated, a part of the salt is decomposed by the water into hydrochloric acid, which passes away, and zinc oxide, which unites with the rest of the zinc chloride to form a basic salt. The concentrated solution of zinc chloride is powerfully caustic and cannot be filtered through paper. It also possesses strong antiseptic properties, and is sometimes used to preserve wood from decay. If a concentrated solution of zinc chloride is made into a paste with zinc oxide, the mixture becomes warm and soon sets to a snow-white hard mass of an oxy-chloride. If finely powdered glass is added to the mixture, a very hard cement is obtained; such mixtures are employed as a cheap stopping for decayed teeth.

Zinc Sulphide: ZnS.—The zinc sulphide occurring in nature as *blende* is of a yellow or brown colour, but that obtained artificially by precipitating a solution of a zinc salt with ammonium sulphide is a pure white powder. Hydrochloric acid readily dissolves it, with evolution of sulphuretted hydrogen and formation of zinc chloride. Zinc sulphide is not precipitated when sulphuretted hydrogen is led into a solution of a zinc salt acidulated with hydrochloric or sulphuric acid; but the gas throws down all the zinc from a solution of its acetate.

Detection of Zinc Compounds.

If any zinc compound is mixed with sodium carbonate and heated on a piece of charcoal in the inner blowpipe flame, the zinc is reduced, volatilized and burnt, and produces an incrustation on the charcoal which is yellow when hot, and white when cold. Zinc compounds are further characterized by the white precipitate which they give with ammonium sulphide. Zinc may be easily separated from iron, nickel, and cobalt by the addition of caustic soda in excess. Zinc oxide then alone dissolves, and can

afterwards be precipitated as white zinc sulphide by passing sulphuretted hydrogen through the alkaline solution. Zinc hydrate and carbonate dissolve also in caustic potash, in ammonia, or in ammonium carbonate, and produce soluble double compounds.

CADMIUM.

Chemical Symbol: Cd.—*Atomic Weight*: 112.

Like indium, cadmium is nearly always found associated with zinc in nature, but zinc ores usually contain far more cadmium than indium—often as much as five per cent. Cadmium is obtained as a bye-product in the extraction of zinc, and as it is more volatile than this metal, is found chiefly in the first portions which come over when the zinc is distilled. Cadmium sulphide is occasionally found as the rare mineral, *greenockite*.

Cadmium is a tin-white metal, of specific gravity 8·6, melting at 315° and boiling at about 770°. Unlike zinc, it is soft at the ordinary temperature, and can be rolled into sheets or drawn into wire. The metal remains unaltered in the air, but burns brilliantly at a red-heat, producing brown vapours of cadmium oxide. It dissolves slowly in hydrochloric or dilute sulphuric acid, with evolution of hydrogen; nitric acid dissolves it more readily.

All compounds of cadmium contain the metal in the form of a diad, in which respect it resembles zinc.

Cadmium Oxide: CdO, is obtained as a brown amorphous powder, soluble in acids, when the metal is heated in the air or when the nitrate is glowed. *Cadmium Hydrate*: $Cd(OH)_2$, is thrown down as a white precipitate on adding caustic soda to a solution of a cadmium salt. The precipitate is insoluble in excess of caustic soda, and so differs from zinc hydrate; it is, however, like the zinc compound, easily soluble in ammonia.

The cadmium salts, with the exception of the sulphide, are all colourless.

Cadmium Sulphate: $3SO_2O_2Cd + 8H_2O$, forms large, colourless, easily soluble crystals. *Cadmium Nitrate*: $(NO_2)_2O_2Cd\ 4H_2O$, crystallizes in deliquescent prisms. *Cadmium Carbonate*: $CO \cdot O_2Cd$, is precipitated as a white powder by adding sodium carbonate to a solution of a cadmium salt. *Cadmium Chloride*: $CdCl_2 + 2H_2O$,

crystallizes in colourless prisms, which effloresce when exposed to the air and are easily soluble in water. *Cadmium Sulphide*: CdS, is thrown down when sulphuretted hydrogen is led into a solution of a cadmium salt as a bright yellow precipitate, which is insoluble in dilute, but dissolves in concentrated hydrochloric acid. It is distinguished from arsenious sulphide, which has a similar colour, by its insolubility in alkaline sulphides, including ammonium sulphide. Cadmium sulphide is used as a stable yellow pigment.

Detection of Cadmium Compounds.

Compounds of cadmium when heated on charcoal in the inner flame of the blowpipe are reduced to the metallic state, but the metal at once volatilizes and burns in the outer flame, producing a brown incrustation of cadmium oxide on the charcoal.

When a current of sulphuretted hydrogen is led through an acid solution of a cadmium salt, a yellow precipitate of cadmium sulphide is produced, insoluble in alkaline sulphides (distinction from arsenic). This reaction serves to separate cadmium from zinc, which is not precipitated from its acid solutions by sulphuretted hydrogen. If ammonia is added to a solution of a cadmium salt, a white precipitate of cadmium hydrate is formed, which dissolves in an excess of the reagent. Caustic soda produces the same precipitate, but does not redissolve it when an excess is added. Cadmium may be separated from copper by boiling the mixed sulphides with dilute sulphuric acid; the cadmium sulphide then dissolves and the cupric sulphide remains behind.

LEAD.

Chemical Symbol: Pb.—*Atomic Weight*: 206·5.

The most important form in which lead occurs in nature is as the sulphide: PbS—the mineral *galena*. Lead is also found in smaller quantities as the sulphate—*anglesite*, as the carbonate—*cerussite*, and less commonly as the chromate, phosphate, and molybdate.

Two processes are chiefly used for the extraction of lead from galena accordingly as the ore is more or less pure. The impure

ores are either roasted and reduced with carbon or else simply smelted with iron. In the latter case the iron unites with the sulphur, for which it has a stronger attraction than the lead, and forms a fusible slag of ferrous sulphide with the impurities, which covers the heavier reduced lead. In the second method—the so-called *air reduction process*—the sulphur is indirectly oxidized by the oxygen of the air. The ore is first carefully roasted in a specially constructed furnace, so that one portion is converted into lead sulphate, another portion into lead oxide, and the rest remains as unchanged lead sulphide. The whole is afterwards well mixed and heated more strongly with exclusion of air, when the sulphur in the unchanged sulphide is burnt by the oxygen contained in the lead oxide and sulphate, and the reduced lead runs from the hearth of the furnace into moulds :—

$$PbS + 2PbO = 3Pb + SO_2.$$
$$PbS + SO_2 \cdot O_2Pb = 2Pb + 2SO_2.$$

Lead when thus smelted often contains silver. If the quantity is sufficient to pay for its extraction,[1] the lead is converted by oxidation into lead oxide, the silver remaining unchanged. This process, called *cupellation*, is performed in an oxidizing reverberatory furnace, of which the German form is shown in fig. 66. This

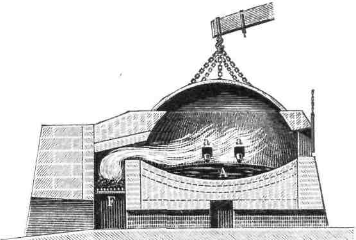


Fig. 66.

furnace consists of a porous clay hearth, on which the argentiferous lead, A, is placed, and which is kept fused by the heated gases

1 *I.e.* about one-tenth per cent.

from the fire, F, while a continuous blast of air is blown through the openings *a*, *a*, over the surface of the metal in order to oxidize the lead to lead oxide. The lead oxide melts as it is produced, and is partly absorbed by the porous clay, but mostly flows away by side openings into vessels provided to receive it. The silver, however, remains unoxidized, and the lead oxide is therefore free from this metal, except towards the end of the operation. Finally, when all the lead has been converted into lead oxide, and the silver is coated with a thin film of the oxide, beautiful iridescent tints are observed on its surface, due to the colours of thin plates; immediately afterwards the bare surface of the molten silver flashes out, and the operation is over. In the English form of cupel furnace, the hearth is made of bone ash, and the cover is not moveable. The lead oxide (litharge), of which large quantities are produced by cupellation, is afterwards again converted into metallic lead by reduction with charcoal or coal.

Two other processes are now largely used for extracting silver from lead, when the quantity is insufficient to pay the expense of cupelling. The first of these, known as *Pattinson's process*, depends upon the fact that when fused argentiferous lead is allowed to cool slowly, the crystals of lead which first separate out are almost entirely free from silver; and if these crystals are removed and the operation repeated several times, a sample of lead is at last obtained which is rich enough in silver to pay for cupelling. A second method, called *Parkes' process*, is based upon the property of zinc to form an alloy with silver, but not with lead. If a small quantity of zinc is added to the molten argentiferous lead, and the mass allowed to cool, the alloy of zinc and silver rises to the surface and can be removed during solidification. The zinc can then be abstracted from this alloy by dissolving it in dilute sulphuric acid, or by distilling it off.

Lead is a lustrous metal of bluish-grey colour, and soft enough to be cut with a knife, and to mark paper. It is malleable and ductile, but possesses little tenacity. The metal has a specific gravity of 11·4, melts at 325°, and volatilizes at a white heat, though it cannot be distilled. Exposed to moist air, it becomes coated with a thin grey layer of the hydroxide and carbonate. Pure water containing air also attacks it and dissolves a small quantity of the lead. But if the water contains traces of certain salts dissolved in it—*e.g.* calcium sulphate—the leaden pipes through which the water passes are not attacked. All lead compounds are

poisonous, especially when dissolved in water, and hence drinking water containing only traces of dissolved lead (probably as its acid carbonate) is injurious to health. The presence of lead in a sample of drinking water may be readily proved by the addition of sulphuretted hydrogen water, or by leading a stream of the gas through it, when if lead is present the water becomes of a brown colour from the lead sulphide formed.

Hydrochloric acid and dilute sulphuric acid scarcely act upon lead, either in the cold or when warmed. Hot concentrated sulphuric acid dissolves lead slightly, but only so slightly that sulphuric acid may be evaporated to a certain strength in leaden dishes (see p. 159). The best solvent for lead is nitric acid, which dissolves it readily, producing lead nitrate and nitric peroxide. From this salt, or from a solution of lead acetate, zinc precipitates metallic lead. The lead is then deposited in lustrous crystalline plates, and, as the metal in this form possesses some similarity with leaves and boughs, it is sometimes called a 'lead-tree.'

Lead unites with oxygen (not with sulphur or the halogens) in three proportions, and produces the compounds—*lead suboxide*: Pb_2O, *lead oxide*: PbO, and *lead peroxide*: PbO_2. Two other known oxides are *red-lead*: Pb_3O_4, and the *sesqui-oxide*: Pb_2O_3; but these may be considered as compounds of lead oxide and lead peroxide.

Lead Suboxide: Pb_2O.—This compound, which is only of scientific interest, is a dark-grey powder, and is produced when lead oxalate is heated to 300° in an oil-bath as long as gas is given off. The decomposition which the oxalate then undergoes is represented in the equation:—

$$2\left\{\begin{matrix}CO\\CO\end{matrix}\right.O_2Pb = Pb_2O + 3CO_2 + CO.$$

Lead suboxide, when heated in the air, is converted into lead oxide; it does not unite with acids, but is decomposed by them into lead oxide and lead.

Lead Oxide, *Litharge, Massicot*: PbO, occurs as a yellow or reddish powder, or as crystalline scales, according to the method used for its preparation. It easily melts, and solidifies on cooling to a crystalline mass. Lead oxide may be obtained by heating either lead hydrate, carbonate, or nitrate, or by the oxidation of molten lead in the air. Most of the litharge brought into trade is derived from the cupellation of argentiferous lead.

Lead oxide is insoluble in water, but dissolves easily in nitric or acetic acid. It is a powerful base, and as most of its salts are insoluble in water, a solution of the soluble acetate is used in the laboratory for the detection of acids.

Litharge is largely used in the arts; considerable quantities are used in the manufacture of flint-glass, and as a cheap glaze for stone and earthenware. Nearly all other lead compounds are prepared from it—*e.g.* lead acetate and nitrate, red-lead, lead-plaster, &c.

Lead Hydrate: $Pb(OH)_2$, is produced as a white, voluminous precipitate, when a solution of lead acetate is mixed with a large excess of caustic soda, until the solution is strongly alkaline, and until a portion of the hydrate has been redissolved by the soda. If a smaller quantity of caustic soda is used than is required to completely precipitate the lead, the lead hydrate is mixed with basic lead acetate; and as sodium acetate itself has an alkaline reaction, the liquid must be strongly alkaline before the soda is in excess. Lead hydrate preserves its white colour when washed and dried. It is quite insoluble in water, but unites with acids more readily than lead oxide, and even attracts carbonic acid from the air. When heated it loses water and yields lead oxide.

Red-lead: $Pb_3O_4 = 2PbO,PbO_2$.—If litharge (lead oxide) is heated in the air to about 400°, but not much above, it absorbs oxygen, and is converted into a bright brick-red crystalline powder. This substance is called red-lead or *minium*, and is used both as a pigment and for a number of other technical purposes. This oxide cannot unite with acids and form salts like lead oxide; and although dilute nitric acid acts upon it even in the cold, it only abstracts lead oxide from it, and leaves brown lead peroxide behind. Red-lead evolves chlorine when warmed with hydrochloric acid, owing to the lead peroxide which it contains. When strongly heated it loses oxygen and is converted into yellow lead oxide.

Lead Sesquioxide: Pb_2O_3. (See Appendix.)

Lead Peroxide: PbO_2.—The preparation of this substance from red-lead by the action of dilute nitric acid has just been described. When repeatedly boiled and washed with water and dried, it remains as a brown amorphous powder, with a purple tinge—

whence it is sometimes called the puce-coloured oxide of lead. Lead peroxide has also been found native in black six-sided prisms as plattnerite. No solvent is known for lead peroxide; like manganese peroxide, which it resembles in other points, it is not attacked by nitric acid. When warmed with hydrochloric acid it evolves chlorine; and when heated alone or with sulphuric acid oxygen is given off, and in the latter case, white insoluble lead sulphate remains behind. It unites with dry sulphurous anhydride, with considerable evolution of light and heat, and produces the same substance (p. 152). If lead peroxide is warmed with nitric acid, and finely powdered sugar gradually added, the sugar is oxidized to carbonic acid and water by a half of the oxygen contained in the peroxide, and a clear solution of lead nitrate is soon obtained.

Salts of Lead.—All the salts of lead contain the metal as a diad, and correspond to lead oxide; none have yet been prepared containing lead in the tetrad form, although it is possible that a tetrachloride corresponding to the peroxide might be produced by the action of hydrochloric acid on the peroxide; but if produced it is so unstable that its isolation is exceedingly difficult.

Most of the lead salts are insoluble in water. Those which dissolve in water include the nitrate and chlorate, as well as the acetate. Although the acetate belongs strictly to organic chemistry, it is the most important soluble lead salt, and may well be included with the inorganic compounds. Many salts of lead are largely used both in the arts and in medicine. All lead compounds, and especially those which are soluble in water, are very poisonous. The soluble compounds are characterized by their sweet taste.

Lead Sulphate: $SO_2 \cdot O_2Pb$, occurs in nature as the mineral *anglesite*, and may be prepared artificially by precipitating a soluble lead salt with dilute sulphuric acid or with a solution of a sulphate. It is only very slightly soluble in water and dilute acids, but hot concentrated sulphuric acid dissolves not inconsiderable quantities of it. Strong hydrochloric acid converts it partially into lead chloride, with the liberation of the corresponding quantity of sulphuric acid. Lead sulphate dissolves readily in basic ammonium tartrate. Ammonium sulphate also forms a soluble crystalline double salt with it, which is, however, decomposed by water, with separation of lead sulphate.

Lead Nitrate : $(NO_2)_2O_2Pb$, is obtained by dissolving lead or lead oxide in a slight excess of nitric acid, and crystallizes from the solution containing free acid as colourless, transparent, hard octahedra, without water of crystallization. It is soluble in water, but insoluble in strong nitric acid, by which it is precipitated from its concentrated aqueous solution. If the aqueous solution is boiled with powdered lead oxide, some of this substance dissolves and produces a difficultly soluble basic salt of the composition : $NO_2 \cdot OPb(OH)$, which crystallizes out on cooling. Lead nitrate decomposes when heated into lead oxide, oxygen, and nitric oxide (p. 196).

Lead Phosphate : $(PO)_2O_6Pb_3$, is thrown down as a white precipitate when sodium phosphate is added to a solution of a lead salt. It is insoluble in water and acetic acid, and forms double compounds with other lead salts—*e.g.* the nitrate and chloride. The mineral *pyromorphite* is a double compound of lead phosphate and chloride : $3(PO)_2O_6Pb_3 + PbCl_2$, and is isomorphous with apatite (p. 396).

Lead Silicates.—Silica and lead oxide may be fused together in almost any proportion, producing a vitreous mass of varying composition, which is an essential constituent of flint or lead-glass, and strass (p. 403). A lead silicate of definite composition has not yet been prepared.

Lead Carbonate : $CO \cdot O_2Pb$.—The normal salt of the above composition is found in nature as the mineral *cerussite*, isomorphous with arragonite, and may be prepared artificially as a white powder, insoluble in water, when a solution of lead nitrate is precipitated with ammonium carbonate.

Basic Lead Carbonate, White Lead : $2CO \cdot O_2Pb + Pb(OH)_2$. —Far more important than the preceding compound is a basic carbonate of lead, very largely used in the arts as a white pigment. White lead is manufactured by a variety of methods, of which the following two are the most important.

The *French or English process* depends upon the fact that a stream of carbonic acid, when led into a solution of basic lead acetate, precipitates the whole of the lead oxide which the salt contains in excess of the normal compound as white lead. Finely

powdered litharge (lead oxide) is boiled with dilute acetic acid until no more is dissolved, when the normal acetate is first obtained, and then the basic salt. On passing a stream of carbonic acid through the clear solution, a precipitate of white lead is produced with a solution of the normal acetate. This solution can be again converted into the basic acetate by boiling with litharge, and from this carbonic acid again throws down a further quantity of white lead, and so on. Thus, with a small quantity of acetic acid a large quantity of white lead can be obtained.

A second and older method, called the *Dutch process*, because first carried on in Holland, consists also in decomposing a basic lead acetate with carbonic acid, but the arrangement by which this reaction is brought about is different. Plates of lead coiled into a spiral or cast leaden gratings are placed in earthenware pots containing a layer of strong vinegar at the bottom. The pots are then loosely closed with a leaden lid and imbedded in horse-dung or spent tan. After several weeks the vessels are withdrawn and opened, when the leaden plates are found to be strongly corroded and covered with a loose layer of white lead. This is removed, and the plates returned to the pots until they are completely corroded away. The process by which the white lead is produced is a simple one. The warmth produced by the decomposition of the dung or spent tan gradually evaporates the vinegar which attacks the lead, and, in the presence of the oxygen of the air, produces basic lead acetate. The acetate is then decomposed as fast as it is produced by the carbonic acid evolved during the putrefaction of the dung or spent tan, producing white lead, which remains loosely adhering to the leaden plates. White lead prepared in this way is more highly valued as a pigment than that obtained by any other process. The colour is purer and it covers better.

Lead Acetate, *Sugar of Lead*: $\bar{A}_2 \cdot O_2Pb + 3H_2O = (C_2H_3O)_2O_2Pb + 3H_2O$.[1]—Normal lead acetate is obtained by dissolving litharge in a small excess of acetic acid, and crystallizes in colourless, transparent, glistening prisms when the solution is evaporated down. Of all lead salts it is the most solùble in water; it also dissolves in spirits of wine of ordinary strength.

[1] The abbreviated symbol $\bar{A}$ here stands for the radical of acetic acid (acetyl) : C_2H_3O, and has the same relation to acetic acid : $\bar{A} \cdot OH$, as nitryl : NO_2, has to nitric acid : $NO_2 \cdot OH$. $\bar{A}$ is, however, employed by many chemists to represent $C_2H_3O_2$.

If a solution of the normal acetate is boiled with lead oxide it combines with this substance and produces various basic acetates, of which those containing the greatest quantity of the oxide are insoluble in water. The monobasic acetate of the composition: $\bar{A}_2 \cdot O_2Pb + Pb(OH)_2 = \bar{A}.OPb(OH)$, is easily soluble in water and reacts alkaline. It parts with one half of its lead when carbonic acid is led through its solution.

Lead Chromate: $CrO_2 \cdot O_2Pb$, is found in nature as the mineral *crocoisite*, and may be obtained as a bright yellow powder by precipitating a soluble lead compound with potassium chromate or dichromate. This precipitated lead chromate when washed and dried is largely used as a yellow pigment under the name of *chrome-yellow*. It melts when heated, and at higher temperatures evolves oxygen. If chrome-yellow is digested with caustic potash or soda, or if boiled with normal potassium chromate, it loses chromic acid and is converted into a basic lead chromate of a bright red colour and the composition: $CrO_2 \cdot O_2Pb + PbO$. This substance is the *chrome-red* of commerce, and is also largely used as a pigment.

Lead Chloride: $PbCl_2$.—This salt, which is only slightly soluble in cold water but more in hot water, is deposited as a heavy white precipitate when hydrochloric acid or a soluble chloride is added to a solution of lead acetate. It crystallizes from its hot saturated solution in colourless lustrous scales or needles. When strongly heated, the salt melts, and solidifies on cooling to a horny mass which may be cut with a knife.

Lead chloride unites with lead oxide in varying proportions and produces different basic chlorides or oxychlorides. One of these is *Cassel yellow*; it is prepared by heating a mixture of litharge and sal-ammoniac, and is used as a pigment. Another oxychloride, of the composition: $PbCl_2,PbO$, is the mineral *matlockite*. If an aqueous solution of lead chloride is boiled with lead hydrate, the whole of the former salt is precipitated as insoluble oxychloride.

Lead Iodide: PbI_2, is thrown down as a pale yellow precipitate when potassium iodide is added to a solution of lead acetate. It is nearly insoluble in cold water, but boiling water dissolves it slightly. This hot solution is colourless, but on cooling deposits

the dissolved lead iodide in lustrous golden scales. Lead iodide forms a double compound with potassium iodide.

Lead Oxy-cyanide: $PbCy_2 \cdot 2PbO$, is a white precipitate obtained by adding ammonium cyanide to lead acetate. The normal cyanide: $PbCy_2$, has not been isolated.

Lead Sulphide: PbS, occurs in nature as *galena*, the most abundant ore of lead. Galena is found either in compact masses of a grey colour, or else crystallized as cubes, usually with subordinate faces of the octahedron.

The same compound may be obtained as a black amorphous precipitate by leading a stream of sulphuretted hydrogen into a solution of a lead salt. The precipitate retains its colour when dry, and if heated out of access of air, melts without decomposition; but if roasted in the air both sulphur and lead undergo oxidation, and there are produced sulphurous anhydride with lead oxide and sulphate. Lead sulphide is scarcely attacked by hydrochloric acid. Dilute nitric acid dissolves it with formation of lead nitrate and free sulphur. Concentrated nitric acid converts it into the white sulphate, as the sulphur is then oxidized.

Numerous double sulphides of lead and other metals, especially antimony, are found in nature; the minerals *zinkenite*, *jamesonite*, and *boulangerite*, are all double sulphides of lead and antimony in varying proportions.

Besides the salts of lead oxide in which this compound plays the part of a base, others are known in which it is combined with strong bases as an acid. These compounds—called *plumbates*—are produced by digesting lead hydrate with the aqueous alkalies or with lime- or baryta-water, in which the hydrate easily dissolves. The salts so obtained—e.g. *potassium plumbate*, whose constitutional formula is: $PbO(OK)_2$—are difficult to prepare, as they are stable only in presence of an excess of alkali.

Alloys of Lead.—Metallic lead is not only used alone for the manufacture of water-pipes, for covering roofs, and for sulphuric acid chambers, but it is also a constituent of many important alloys. One of these is *type-metal*, an alloy of lead and antimony. German type-metal contains from 10 to 25 parts of antimony to 100 parts of lead, while that used in England contains about 30 parts of antimony

and 30 parts of tin to 100 parts of lead, and sometimes a little copper as well. The larger the quantity of antimony, the harder and more brittle is the alloy produced. The addition of a small quantity of arsenic (at most 0·8 per cent.) to lead makes it suitable for the manufacture of *shot*. The alloys of lead and tin are described under the latter metal.

Detection of Lead Compounds.

Scarcely any other metal can be so easily detected and separated as lead. Any compound of lead when mixed with sodium carbonate and heated on charcoal in the reducing flame of the blowpipe yields small soft globules of metallic lead, which mark paper, and which are converted into yellow lead oxide in the oxidizing flame. In the borax bead, as in other forms of molten glass, lead oxide dissolves without imparting any colour.

Sulphuretted hydrogen when passed through a neutral or acid solution of a lead salt precipitates black lead sulphide. The same solution gives a white precipitate of lead sulphate with dilute sulphuric acid, a white precipitate of lead chloride with hydrochloric acid, which dissolves in hot water, and crystallizes out in needles on cooling, a yellow precipitate of lead iodide with potassium iodide, and a white precipitate of lead hydrate with caustic soda, soluble in excess of the reagent. Ammonia produces no precipitate when added to a solution of lead acetate or only a slight one, after some time, but at once throws down basic lead nitrate when added to a solution of lead nitrate. The yellow precipitate which is obtained when potassium dichromate is added to a lead salt is also produced with a bismuth salt, but lead chromate may be distinguished from the bismuth salt by its solubility in caustic soda.

The separation of lead from the other metals precipitated from their acid solutions by sulphuretted hydrogen is best effected by the addition of sulphuric acid and alcohol. Lead sulphate is slightly soluble in water, less in dilute sulphuric acid, and insoluble in alcohol.

THALLIUM.

Chemical Symbol: Tl.—*Atomic Weight*: 204.

This remarkable element occupies an altogether anomalous position among other metals, for it unites in itself the chemical and physical properties of two groups of metals which are as different as possible from one another. On the one hand it has much similarity with lead and silver, and on the other with the alkali-metals, especially potassium.

It resembles lead in possessing nearly the same atomic weight and specific gravity, and in its difficultly soluble chloride and insoluble iodide. Its sulphate is also difficultly soluble in water, though not to such an extent as lead sulphate; its neutral solutions are precipitated by sulphuretted hydrogen, and the metal is set free from its soluble salts by metallic zinc.

It differs from lead, but resembles silver and potassium, in its atomicity, which in the above compounds is always unity, and is similar to potassium in many other points. Although it does not decompose water like potassium, it easily dissolves in water containing air, and produces thallium hydrate, which is readily soluble in water, and of which the solution reacts strongly alkaline. Still more remarkable is the fact that a metal so similar to lead as thallium should possess a carbonate soluble in water, and even reacting alkaline. Twenty-five years ago, when thallium was unknown, it was universally held that only the alkali-metals yield soluble carbonates, and it was not thought possible that the carbonate of a heavy metal could be soluble in water; still less was it imagined that the sulphate of a heavy metal could displace potassium sulphate in common alum without changing the physical properties of the salt. We now know that thallous carbonate is soluble in water, giving an alkaline solution, and that thallous sulphate can unite with aluminium sulphate and produce a true alum. And further, thallous chloride, just like potassium chloride, can unite with platinum chloride, and produce a double salt insoluble in water.

Thallium is a rare element, and although present in many ores and mineral waters, is only found in minute quantities. The mineral richest in thallium is *crookesite* (called after Crookes, the discoverer of the element), which contains about 18 per cent. of

the metal, but which is extremely rare. Thallium is best prepared from some varieties of iron or copper pyrites. When pyrites containing traces of the metal is used for the manufacture of sulphuric acid, the thallium passes over with the gases, and is then contained in the flue-dust or in the deposit which forms on the floor of the leaden chambers. This flue-dust or deposit when boiled with dilute sulphuric acid yields an impure solution of thallous sulphate, which when evaporated down and mixed with hydrochloric acid gives a precipitate of thallous chloride. This precipitate is filtered off, well washed with cold water and then decomposed with concentrated sulphuric acid, which converts it into thallous sulphate. On dissolving this salt in water, and dipping a plate of zinc (free from lead) into it, the thallium is precipitated as a crystalline, spongy mass, which is then pressed together and fused in a crucible.

Thallium so obtained is of a tin-white colour when freshly cut; it is very soft, and, like lead, may be cut with a knife or even scratched with the nail, and easily marks paper. It has a specific gravity of 11·9, melts at 290°, and volatilizes at a red heat. Thallium readily oxidizes when exposed to the air and becomes covered with a thin layer of oxide, but, notwithstanding its strong attraction for oxygen, it does not decompose water even at the boiling temperature. It preserves its bright surface under water which has been freed from dissolved air by boiling, and is therefore best kept under this liquid. But if the water is exposed to the air the thallium gradually becomes converted into thallous hydrate and thallous carbonate, both of which dissolve in the water. It easily dissolves in dilute nitric or sulphuric acid, but less readily in hydrochloric acid on account of the insolubility of its chloride.

With oxygen, sulphur, and the halogens, thallium forms two series of compounds—the thallous and thallic compounds. In the former it is a monad element, and in the latter a triad. The former (thallous) series of compounds are the more stable, and thallous oxide is a much stronger base than thallic oxide. All thallium compounds are poisonous.

If thallium is allowed to remain for a long time under water which has access to air or oxygen free from carbonic acid, the aqueous solution becomes strongly alkaline from the *thallous hydrate*: TlOH, which has been produced. When this solution is evaporated down, the hydrate crystallizes out in yellow rhombic prisms with 1 molecule of water. The same substance may be

more easily obtained by precipitating a solution of thallous sulphate with baryta-water, filtering off the barium sulphate produced, and evaporating the clear solution. It is soluble both in water and alcohol. When heated to 100° it decomposes into water and *thallous oxide*: Tl_2O, which forms a black powder, melting at about 300° to a dark yellow liquid. The oxide attracts moisture from the air and is again converted into the hydrate.

Thallous Sulphate: $SO_2(OTl)_2$, crystallizes in colourless rhombic prisms isomorphous with potassium sulphate, and unites with aluminium sulphate to form *thallium-alum*: $\begin{matrix} SO_2 \\ SO_2 \end{matrix}\Big\} \begin{matrix} O_3Al \\ OTl \end{matrix}$ + $12H_2O$ (p. 424). An acid sulphate: $SO_2\Big\{\begin{matrix} OH \\ OTl \end{matrix}$ is also known.

Thallous Phosphate: $PO(OTl)_3$.—If a neutral solution of a thallous salt is mixed with sodium phosphate and a few drops of ammonia added, thallous phosphate soon begins to crystallize out, and afterwards nearly fills the vessel. The crystals are long, glistening prisms, of the above composition, and almost insoluble in water containing a trace of ammonia.

Thallous Carbonate: $CO(OTl)_2$, is obtained by saturating a solution of thallous hydrate with carbonic acid, and crystallizes in colourless lustrous prisms when the solution is evaporated down It is tolerably easily soluble in water, and the solution reacts alkaline. It loses carbonic acid when heated, and is converted into thallous oxide.

Thallous Chloride: TlCl, is thrown down as a white curdy precipitate when a solution of a thallous salt is mixed with hydrochloric acid. It is scarcely soluble in cold water, but dissolves more readily when heated. It easily melts when heated and then volatilizes. Thallous chloride when mixed with platinic chloride forms a yellow insoluble double chloride of the composition: $2TlCl,PtCl_4$, corresponding to the compound of potassium and platinic chlorides.

Thallous Iodide: TlI, like lead and silver iodides, is nearly insoluble in water, and is produced as a yellow amorphous precipitate when potassium iodide is added to a solution of a thallous salt.

Thallous Sulphide: Tl_2S, is obtained as a black precipitate when excess of ammonium sulphide is added to a solution of a thallous salt, and is insoluble in excess of the reagent. Sulphuretted hydrogen produces the same precipitate in a solution of thallous acetate.

Thallic Compounds.—Thallic hydrate and oxide, unlike the corresponding thallous compounds, are insoluble in water, but are dissolved by acids to form soluble thallic salts. *Thallic hydrate*: $TlO(OH)$, is produced as a brown amorphous powder when freshly precipitated thallous chloride is digested with an excess of sodium hypochlorite. At 100° it breaks up into water and *thallic oxide*: Tl_2O_3, a black powder insoluble in water, but dissolving in hydrochloric acid to form thallic chloride. When heated with concentrated sulphuric acid, oxygen is given off and thallous sulphate remains behind; when heated alone it partially breaks up into thallous oxide and oxygen.

Thallic Sulphate: $(SO_2)_3O_6Tl_2''' + 7H_2O$, crystallizes in colourless thin scales when a solution of thallic hydrate in dilute sulphuric acid is evaporated down. It loses only 6 molecules of water when heated to 220°, and is decomposed by water even in the cold, with separation of thallic hydrate. It forms a difficultly soluble double salt with potassium sulphate, which, however, is not a true alum.

Thallic Chloride: $TlCl_3$, is produced when thallous chloride is gently heated in a stream of chlorine, or when thallic hydrate is dissolved in hydrochloric acid. On evaporating its solution it crystallizes in easily soluble, deliquescent prisms, which decompose, when heated, into thallous chloride and free chlorine.

Thallic Sulphide: Tl_2S_3, may be obtained by fusing thallium with an excess of sulphur. It then forms a black soft mass, which easily melts, and is brittle at low temperatures.

Detection of Thallium Compounds.

The compounds of thallium possess such characteristic properties, that it is an easy matter to detect them, and to separate them from the compounds of other metals. The non-precipitation of thallium compounds by sulphuretted hydrogen from their acid

solutions, the solubility of thallous sulphate in hot water, the insolubility of the chloride and iodide, and the solubility of thallous hydrate and carbonate in water, offer the best means of detection and separation.

Minute traces of thallium can be readily recognized with the spectroscope; its spectrum consists of a single intense green line (see table). It was this property of thallium which led to its discovery, and from which it derived its name (θάλλος = a green twig).

BISMUTH.

Chemical Symbol: Bi.—*Atomic Weight*: 208.

Bismuth is only sparsely distributed in nature, and nearly always occurs in the free state. From the earthy impurities which accompany it, the metal is separated either by simply melting it in inclined iron tubes, or else by roasting in the air, and then heating with carbon and a slag in suitable crucibles. Commercial bismuth always contains traces of other metals, including arsenic. It may be purified by fusion with nitre, which converts the arsenic into potassium arsenate and oxidizes other impurities. To prepare pure bismuth, a solution of its nitrate is precipitated with much water, which gives an insoluble basic nitrate, and this, when washed, dried, and reduced with a mixture of sodium carbonate and charcoal, yields the pure metal.

Bismuth is a greyish-white metal, with a reddish tinge; it is brittle, and can therefore be easily powdered, and crystallizes very easily. If bismuth is fused in a crucible, and when partly solidified, the crust at the top broken, the still liquid metal poured out, and the crucible broken open when cold, its sides are found covered with beautiful iridescent crystals of bismuth, just as crystals of monoclinic sulphur are obtained in the same way. The colour of the crystals is due to a thin layer of oxide, with which the metal becomes covered when the air enters the crucible. The crystals are rhombohedra, the angle of which so closely approaches that of the cube, that bismuth was formerly thought to crystallize in the regular system.

Bismuth has a specific gravity of 9·8, and melts at as low a temperature as 268°; it shares with water the property of expanding considerably on passing from the liquid to the solid state. At high

temperatures it volatilizes, and may be distilled in hydrogen. When heated strongly in air, it burns yielding the yellow oxide. Hydrochloric acid does not attack the metal, and sulphuric acid scarcely dissolves it, but it is at once dissolved by nitric acid, or by aqua regia, and converted into bismuth nitrate or chloride respectively.

Bismuth unites with oxygen in three proportions and forms the compounds bismuth suboxide: Bi_2O_2, bismuth oxide: Bi_2O_3, hypobismuthic oxide: Bi_2O_4, and bismuth pentoxide or bismuthic anhydride: Bi_2O_5. Of these, bismuth oxide is the only important compound.

Bismuth Suboxide: BiO, separates as a black precipitate when caustic soda is added to a mixture of bismuth chloride and stannous chloride. By the action of the caustic soda, stannous hydrate and bismuth hydrate are first produced, and the former then abstracts oxygen from the latter, forming stannic hydrate, which remains dissolved in the excess of soda, and bismuth suboxide. Like other suboxides, it is converted by acids into a bismuth salt and free bismuth.

Bismuth Oxide: Bi_2O_3, remains as a yellow powder, similar to lead oxide, when basic bismuth nitrate is heated to low redness. It melts at a higher temperature, and then solidifies to a crystalline mass on cooling. It dissolves easily in hydrochloric, nitric, or sulphuric acid, producing the corresponding bismuth salts.

Bismuth Hydrate: $Bi(OH)_3$, is thrown down as a white precipitate when a solution of a bismuth salt is mixed with caustic soda. It dissolves easily in acids, but not in an excess of caustic soda. When dry it forms a white powder, which is converted into yellow bismuth oxide on heating.

Bismuthic Acid: $Bi_2O_5 + H_2O$, which is a very feeble acid, is obtained as a red heavy powder when chlorine is led through dilute caustic soda containing white bismuth hydrate in suspension, and is afterwards freed from alkali by washing with a dilute acid, and dried over sulphuric acid. If heated to 120° the

Bismuthic Anhydride: Bi_2O_5, remains as a red powder. This, if heated to 250°, yields the *Hypobismuthic oxide*: Bi_2O_4, a brownish yellow solid, which is reduced at 305° to Bi_2O_3.

Bismuth oxide, like other sesquioxides, is only a weak base, and is partly separated from its salts by water, which in this case plays

the part of a base. Only a small number of bismuth salts are known.

Bismuth Nitrate: $(NO_2)_3O_3Bi + 5H_2O$.—Metallic bismuth dissolves easily in nitric acid, with evolution of nitric peroxide, and on evaporating the clear solution large colourless crystals of bismuth nitrate of the above composition separate out. The salt dissolves in a small quantity of water, especially if a little nitric acid is added, but a large quantity decomposes the salt like antimony trichloride, and produces a white crystalline precipitate consisting of a mixture in varying proportions of three *basic bismuth nitrates* of the composition :—

$$\left.\begin{matrix} NO_2 \\ NO_2 \end{matrix}\right\} O_2{\cdot}Bi_2 \left\{\begin{matrix} (OH)_2 \\ O \end{matrix}\right. ; \left.\begin{matrix} NO_2 \\ NO_2 \end{matrix}\right\} O_2{\cdot}Bi{\cdot}OH \text{ ; and } NO_2{\cdot}O{\cdot}Bi_2 \left\{\begin{matrix} OH \\ O_2 \end{matrix}\right. .$$

It is largely used in medicine in cases of cholera and chronic diarrhœa, and is also employed as a cosmetic.

Bismuth Chromate is deposited as a bright yellow precipitate, resembling lead chromate, when a solution of bismuth nitrate is mixed with one of potassium chromate. It is distinguished from the lead salt by its insolubility in a large excess of caustic soda.

Bismuth Chloride: $BiCl_3$.—If bismuth is heated in a retort and dry chlorine led into it, it burns and forms bismuth chloride, which distils over as a viscid liquid, and solidifies on cooling to a white crystalline mass. It boils at about 430°. The same compound may also be obtained by dissolving bismuth in aqua regia, evaporating to dryness, and distilling. It deliquesces in the air, and is decomposed by water, like the nitrate, producing a white crystalline powder of insoluble *basic bismuth chloride* (*bismuth oxychloride*) : $BiOCl$.

Bismuth Sulphide: Bi_2S_3, occurs in nature as the mineral *bismuthine*, and is thrown down as a dark-brown precipitate when sulphuretted hydrogen is led into a solution of a bismuth salt. It may also be prepared by fusing together bismuth and sulphur.

Detection of Bismuth Compounds.—Bismuth, like lead, may be easily reduced by heating any of its compounds with sodium carbonate on charcoal in the reducing flame of the blowpipe, and the globules of metal are easily oxidized in the outer flame to yellow

bismuth oxide, resembling lead oxide. The globules of reduced bismuth are, however, brittle, while those of lead are soft and malleable.

Solutions of bismuth salts give, like lead, a black precipitate with sulphuretted hydrogen, but a solution of a bismuth salt gives a white precipitate of a basic salt when poured into water, and yields no precipitate when mixed with sulphuric or hydrochloric acid. Further, the precipitate of bismuth hydrate obtained with caustic soda is not soluble in excess.

Bismuth oxychloride may be distinguished from the corresponding compound of antimony by its insolubility in a strong solution of tartaric acid, in which the latter easily dissolves.

TIN.

Chemical Symbol: Sn.—*Atomic Weight*: 118.

Tin belongs to those few metals which have been known from the earliest times, and this is all the more remarkable as the metal never occurs native, and its ores are only sparingly found in nature. For the extraction of tin only one mineral is used—viz. *cassiterite* or *tinstone*, consisting of stannic oxide, with the composition: SnO_2. This mineral is found in large quantities in Cornwall, in the Erzgebirge (Saxony and Bohemia), and other European localities, as well as in Banca, the Malay Peninsula, Peru, and Australia. The extraction of the metal from its ore is a very simple process. The tin-stone is first roasted to get rid of arsenic and sulphur, then stamped to powder and washed with water to remove the lighter earthy impurities, and finally smelted with anthracite or powdered charcoal in a reverberatory furnace. The reduced tin, which sinks to the bottom of the hearth, is then withdrawn and refined by re-melting in iron pots and stirring with a green pole. Commercial tin is always more or less impure, and often contains arsenic. The pure metal is easily obtained by heating pure stannic oxide and charcoal in a crucible, with the addition of a little borax or some similar flux.

Tin is a white metal, resembling silver, with a brilliant lustre, and a specific gravity of 7·3. It is soft and very malleable, so that it can be hammered out into thin foil (tin-foil), but possesses little tenacity. Up to 100° its malleability increases, but when heated

above this it becomes less malleable, and is even brittle at 200°. Advantage is taken of this property to produce what is called *grain-tin—i.e.* tin which has been heated to about 200° and broken to pieces under the hammer. Tin melts at 228°, and when broken shows a crystalline fracture. It is well known that a bar of tin when bent emits a peculiar noise—the so-called *cry of tin*, which is probably produced by the friction of the crystals of tin over one another. Commercial tin, when grasped in the hand, imparts to the skin a peculiar odour, not possessed by the metal itself.

At the ordinary temperature, tin remains unchanged in the air, but becomes covered with a thin crust of white oxide when exposed to the air in the fused state. At a white heat it burns with a bright white light. Hot concentrated hydrochloric acid dissolves tin with evolution of hydrogen and produces stannous chloride; the metal also dissolves in hot strong sulphuric acid, forming stannous sulphate and giving off sulphurous acid. Aqua regia dissolves the metal and forms stannic chloride. Ordinary concentrated nitric acid oxidizes the metal, with the production of large quantities of brown fumes and formation of white stannic oxide, insoluble both in water and nitric acid. Finally, tin is also dissolved when heated with caustic potash; hydrogen is then set free and a solution of potassium stannate produced.

The compounds of tin are divided into two classes—the stannous and the stannic compounds. In the former the metal is a diad in the latter a tetrad.

Stannous Compounds.

Stannous Oxide: SnO.—The precipitate of white stannous hydrate obtained when caustic soda is added to stannous chloride easily dissolves in an excess of soda, and produces sodium stannite. If the alkaline solution is boiled it undergoes decomposition, and a black crystalline precipitate of stannous oxide is thrown down. After washing and drying, the compound remains unchanged in the air. If, however, the solution of stannous chloride is precipitated with sodium carbonate instead of caustic soda, the white *stannous hydrate*: $Sn(OH)_2$, which is now produced (together with free carbonic acid) behaves differently and oxidizes in the air to stannic oxide.

The oxysalts of stannous oxide are but little known. *Stannous sulphate*: $SO_2 \cdot O_2Sn$, may be prepared by dissolving tin in hot con-

centrated sulphuric acid, and is then deposited in crystalline plates when the solution cools. When its aqueous solution is boiled it undergoes decomposition, with formation of a basic salt.

Stannous Chloride : $SnCl_2$.—Tin when heated in dry hydrochloric acid gas is gradually converted into a white crystalline mass of stannous chloride, which melts at 250° and sublimes at a higher temperature. Stannous chloride is, however, usually prepared by dissolving tin in hydrochloric acid, an operation which may be considerably accelerated by the addition of a few scraps of platinum foil or of a few drops of platinum chloride, which is at once reduced to metallic platinum. The contact of the platinum with the tin makes the latter far more electro-positive and causes it to dissolve more quickly.[1] On evaporating the solution of stannous chloride the salt crystallizes out with two molecules of water as the compound : $SnCl_2 + 2H_2O$. This salt is manufactured on a large scale, and is brought into trade under the name of *tin-salt.* The readiness with which stannous chloride passes into stannic chloride makes it a powerful reducing agent. Mercuric chloride is at once reduced by it to mercurous chloride, and on warming to metallic mercury, while the stannous chloride becomes stannic chloride. An aqueous solution of stannous chloride becomes turbid when exposed to the air, and gradually deposits a basic chloride.

Stannous chloride is largely used in dyeing and for purposes of reduction.

Stannous Sulphide : SnS.—On heating a mixture of tin-filings with an excess of sulphur in a closed crucible the two substances unite and form dark-grey, lustrous scales of stannous sulphide. The same compound is obtained as a dark-brown precipitate when sulphuretted hydrogen is led into a solution of stannous chloride. The precipitate dissolves in hydrochloric acid with evolution of

[1] The action of the platinum, which is deposited in a finely divided state on the tin, may be thus explained. Each particle of the platinum forms a galvanic couple with a corresponding particle of tin, and a series of tiny electric currents circulate between the particles of the two metals and the liquid in their neighbourhood. The production of these currents necessitates a more rapid solution of the tin than when the platinum is absent, and they are consequently not produced. Other similar *couples*, as this arrangement has been called, are also occasionally used. Thus, a copper-zinc couple, prepared by treating zinc foil with a very dilute solution of copper sulphate, reduces many substances which zinc alone does not attack, or only very slowly.—ED.

sulphuretted hydrogen, but is insoluble in pure, freshly prepared ammonium sulphide, and is so distinguished from stannic sulphide, which at once gives a soluble compound with ammonium sulphide. Stannous sulphide at once dissolves in ordinary yellow ammonium sulphide, because this compound contains dissolved sulphur, which converts the stannous sulphide into stannic sulphide, and this dissolves in the ammonium sulphide.

Stannic Compounds.

Stannic Oxide: SnO_2, constitutes the mineral *cassiterite* or *tin-stone*, and is found either in compact masses or else in brown quadratic crystals. It may be obtained as a white amorphous powder by burning tin in the air or by heating stannic hydrate. In the crystalline state it is formed when the vapours of stannic chloride and water are led through a red-hot porcelain tube. Stannic oxide is insoluble in acids, and is not attacked when fused with acid potassium sulphate, but may be converted into soluble sodium stannate by fusion with caustic soda or sodium carbonate. Stannic oxide has far more the character of an acid than of a base.

Stannic Hydrates.—At least two hydrates of stannic oxide are known. They are weak acids and very weak bases. If tin is warmed with moderately strong nitric acid, a violent reaction ensues, torrents of nitric peroxide are evolved, and a white insoluble powder of *metastannic acid*, of the probable composition: $(H_2SnO_3)_x$ remains behind. This hydrate is insoluble in water and nitric acid.

Stannic Acid may be conveniently prepared, as a white voluminous precipitate, by adding a solution of sodium carbonate to stannic chloride, or by adding hydrochloric acid to a solution of sodium stannate, a salt which is prepared upon a large scale, for use in calico-printing, by fusing stannic oxide with caustic soda. This acid, though it possesses the same empirical formula as metastannic acid, differs in several of its properties from that substance. Thus, whereas the former dissolves very readily in cold solutions of the alkalies, metastannic acid dissolves only slowly, even on boiling with these reagents. Stannic acid, too, though it resembles metastannic acid in being insoluble in water, differs from

the latter in that it readily dissolves in strong hydrochloric acid or nitric acid. Both hydrates lose water when heated and yield stannic oxide.

It is held by some chemists that metastannic acid is represented by the formula : $(H_2SnO_3)_5$, whilst stannic acid is represented by the simpler formula : H_2SnO_3 ; but this has not been satisfactorily proved.

Stannic acid, when kept for some time under water, becomes insoluble in nitric acid.

Potassium stannate : $SnO(OK)_2 + 3H_2O$, is obtained in the same way as the corresponding sodium compound. It is insoluble in caustic potash, but soluble in water, and is deposited in colourless crystals ; its solution reacts strongly alkaline.

Stannic Chloride : $SnCl_4$.—This volatile liquid, which was formerly known as *Spiritus Libavii fumans*, is obtained when tin is heated in a retort and chlorine passed over it. The distillate when purified by redistillation is a colourless heavy liquid of specific gravity 2·28, and boiling at 114°. It fumes strongly in moist air, almost as much as sulphuric anhydride, and hisses when dropped into water, forming the hydrated salt : $SnCl_4 + 3H_2O$, which crystallizes out. A dilute aqueous solution is decomposed on boiling, with separation of stannic hydrate. A solution of stannic chloride is best obtained by dissolving tin in aqua regia.

Stannic chloride unites with the alkaline chlorides and forms crystalline double salts. The double compound with ammonium chloride : $SnCl_4 + 2NH_4Cl$, is used by calico-printers under the name of *pink-salt*.

Stannic Sulphide : SnS_2, is obtained as a yellow amorphous precipitate when sulphuretted hydrogen is led through a not too acid solution of stannic chloride. It is insoluble in water, but dissolves in strong hydrochloric acid. Hot concentrated nitric acid oxidizes it to stannic hydrate and sulphuric acid. Stannic sulphide possesses the character of a sulpho-acid, and as such easily dissolves in ammonium sulphide, producing soluble *ammonium sulphostannate*, which is easily decomposed by acids with re-separation of stannic sulphide.

Stannic sulphide is prepared in the dry way as golden scales

by heating together tin and sulphur with volatile substances—such as mercury and ammonium chloride—which, by their volatilization, appear to prevent the temperature rising high enough to decompose stannic sulphide into stannous sulphide and sulphur. A solid amalgam of tin is first prepared by adding six parts of mercury to twelve parts of molten tin. This is powdered when cold, mixed with seven parts of flowers of sulphur and six parts of ammonium chloride, and the mixture introduced into a glass flask, the mouth of which is loosely closed by a piece of chalk. The flask is next placed in a crucible surrounded with sand and heated in a good draught to low redness. During the process mercuric chloride, ammonium and stannic chlorides sublime, and at the bottom of the flask is found the stannic sulphide as a loose mass of a golden-yellow colour. The substance so prepared is called *mosaic gold*; it is much more stable than the precipitated sulphide, being scarcely attacked by strong hydrochloric or nitric acid.

Mosaic gold is used for a number of technical purposes, but chiefly for cheap gilding.

More important than the technical applications of the compounds of tin are those of the metal itself, either alone or alloyed with other metals. Considerable quantities of tin are consumed in the manufacture of *tin-plate—i.e.* iron plates coated with a thin layer of tin; copper vessels are tinned internally, and tin-foil is largely used for packing small articles. Tin-foil usually contains traces of copper, which gives it greater tenacity. Not unfrequently it also contains lead, which may produce very deleterious effects if articles of food are packed in the foil. Not only is lead more easily attacked by the acids in the food than tin, but the compounds of lead are far more injurious when introduced into the system than those of tin.

Alloys of Tin.—Different alloys of lead and tin—known as *pewter*—are used for the manufacture of various vessels, and as a basis for the cheaper silver-plated articles; common pewter contains about four parts of tin to one of lead. Common *soft-solder*, chiefly used for soldering tin-plate, is an alloy of 2 parts of tin with 1 part of lead, and melts at about 180°, or of equal parts of the two metals, with a melting-point of about 200°. *Britannia-metal*, a better kind of pewter, is essentially an alloy of about 9 parts of tin with 1 part of antimony. The various alloys of tin with

copper, bronze, &c., will be described under the latter metal; an amalgam of tin is used for silvering looking-glasses. By melting together tin with other easily fusible metals—*e.g.* lead, bismuth, and cadmium—alloys are obtained with very low melting points, and these are largely used in the process of stereotyping. An alloy of 1 part of lead, 1 part of tin, and 2 parts of bismuth (*fusible metal*), melts at 95°; and one consisting of 4 parts of bismuth, 2 parts of lead, 1 part of tin, and 1 part of cadmium (*Wood's metal*), melts at about 68°.

Detection of Tin Compounds.

Tin and antimony are the only elements which are converted by nitric acid into insoluble white oxides; of these the antimony compound may be distinguished by its solubility in a solution of tartaric acid, which leaves the stannic oxide undissolved. Tin itself may be distinguished from antimony by its solubility in hydrochloric acid, which does not attack the latter substance. Stannous compounds, in consequence of the readiness with which they pass into the stannic form, are powerful reducing agents. Stannous chloride precipitates mercury and gold from solutions of their salts, the latter even in the cold. With sulphuretted hydrogen stannous salts give a dark-brown precipitate of stannous sulphide, and the same reagent throws down yellow stannic sulphide when led through solutions of the stannic salts. Both sulphides dissolve in yellow ammonium sulphide. Stannic oxide has more the character of an acid than a base; even stannous oxide possesses faint acid properties, and unites both with strong acids and with strong bases to form salts. Metallic tin, as white malleable globules, may be reduced from its compounds when a compound of the metal is mixed with sodium carbonate and heated on charcoal in the inner blowpipe flame, though the reduction is rather more difficult than that of lead. At the same time, an indistinct white incrustation is formed on the charcoal. Compounds of tin do not tinge a bead of borax, but if a *minute trace* of copper is added, and the bead held in the reducing flame of the blowpipe, it easily becomes of a fine red colour, due to reduced cuprous oxide.

COPPER.

Chemical Symbol: Cu.—*Atomic Weight*: 63·4.

Copper, which has been known from the earliest times, is one of the few metals which possess a decided tint; it is of a bright red colour. The metal is sometimes found in the free state in nature, often well crystallized in octahedra, but more commonly occurs in combination with other elements. The most important ores of copper are: *cuprite* or *red copper ore* (cuprous oxide: Cu_2O), *copper-glance* (cuprous sulphide: Cu_2S), *copper-pyrites* (sulphide of copper and iron: $CuFeS_2$), *purple copper ore* of similar composition, and *tetrahedrite* or *fahlerz* (a mixed sulphide of copper, antimony, arsenic, &c.). Besides these, some oxy-salts of copper are also found in the mineral kingdom, among which may be mentioned the basic carbonates: *malachite* and *azurite*.

The extraction of copper from its oxygen compounds (cuprite, malachite, &c.) is very simple, and analogous to the method used for the reduction of iron. The roasted ores are heated in a blast furnace with some form of carbon, and the reduced copper collects on the hearth under the slag. Only small quantities of copper are extracted from these comparatively rare ores; far more is obtained from copper-pyrites, a double sulphide of copper and iron. The method employed for the separation of copper from these ores is a complex one; a whole series of processes is necessary to completely separate both the iron and the sulphur. These processes, which depend upon the attraction of copper for sulphur and iron for oxygen, consist in alternately roasting and melting the ores. The roasting gradually removes the sulphur and oxidizes the iron, which unites with silica to form a fusible slag. From the residual sulphide, metallic copper is obtained by oxidizing the sulphur, and is toughened by poling whilst molten and covered with charcoal.

Commercial copper is never quite pure, although the impurities are usually insignificant. The pure metal may be obtained as a red powder by heating pure copper oxide in a stream of hydrogen.

Copper melts only at a high temperature, above 1,000°, and burns when heated in the oxy-hydrogen flame. Its specific gravity is about 8·9. The metal takes a good polish, is malleable and ductile, and very tenacious. Bright copper remains unchanged in dry air, but in the presence of moisture becomes covered with a green layer of basic copper carbonate. This green rust of copper

is often called *verdigris*, which is really a basic acetate of the metal. Copper is more rapidly corroded if the surface is moistened with a dilute acid and exposed to the air; it is also attacked by ammonia or a solution of common salt in the presence of air. In the absence of air neither hydrochloric nor dilute sulphuric acid has any action on the metal. Hydrochloric acid does not dissolve it even on heating, but hot concentrated sulphuric acid oxidizes it to copper sulphate, and sulphurous anhydride is set free (p. 151). Unlike iron, zinc, &c., copper can only with difficulty decompose water and form copper oxide and hydrogen; even when copper is heated to redness in steam the decomposition is but slight. If heated to redness in the air copper is coated with a layer of black oxide which separates as scales when the metal is hammered. This copper scale consists chiefly of cupric oxide, but contains some metallic copper and some cuprous oxide.

The best solvent for copper is nitric acid, which dissolves it with evolution of nitric oxide (p. 193), and produces a blue solution of cupric nitrate. Copper is deposited from its solutions by more positive metals—*e.g.* zinc or iron—and also separates in a compact form at the negative pole when an electric current is passed through a solution of the sulphate. The process of producing electrotypes or copies of various objects in copper depends upon this deposition of the metal by an electric current.

Compounds of Copper.

Copper forms with oxygen, sulphur, and the halogens, two series of compounds; the one series contains a single atom of diad copper, and the other 2 atoms of copper which also play the part of a diad. The two series of compounds are called *cupric* and *cuprous* compounds respectively—*e.g.* cupric chloride: $CuCl_2$, and cuprous chloride: Cu_2Cl_2. Of these two series, the cupric compounds are the most important, and shall therefore be first discussed. All compounds of copper are poisonous, especially those which are soluble in water.

Cupric Compounds.

Cupric Oxide, *Black Oxide of Copper*: CuO, is a black amorphous powder, obtained by glowing finely divided copper in the air, or better by heating cupric nitrate. Copper oxide is largely used in organic analysis to oxidize organic substances (p. 289). For this purpose it does not require to be pure, but should be in the form of

scales, and is best prepared from copper scale. A layer of the scale, which has been freed from mechanical impurities, is moistened with nitric acid (containing no chlorine) in a Hessian crucible, then a second layer added and also moistened with the acid until the crucible is about three parts full. The whole is then heated to low redness until all the nitric acid is destroyed and expelled. The nitric peroxide set free during the decomposition of the cupric nitrate suffices to oxidize the copper and cuprous oxide, contained in the scale, to cupric oxide, and if the temperature has not been raised high enough to cause the oxide to cake together, it is obtained in the form of scales well suited for organic analysis.

Cupric oxide may be obtained in the wet way as a black precipitate, by adding hot caustic soda to a hot solution of a cupric salt. Cupric oxide is completely insoluble in water, but readily dissolves in hydrochloric, nitric, or sulphuric acid, without any evolution of gas, then forming the corresponding cupric compounds. When heated in a stream of hydrogen it easily parts with its oxygen and yields metallic copper as a red powder.

Cupric Hydrate: $Cu(OH)_2$.—If a solution of a cupric salt is mixed with an excess of caustic soda at the ordinary temperature, a blue voluminous precipitate of copper hydrate is obtained, in which the copper oxide and water are so loosely combined that the compound is decomposed at 100°, and black cupric oxide even separates slowly at the ordinary temperature. If insufficient caustic soda is employed a basic salt is obtained, which is also of a blue colour, but which remains unchanged when boiled.

Cupric Sulphate, *Blue Vitriol*: $SO_2 \cdot O_2Cu + 5H_2O$, is deposited, when its aqueous solution is evaporated, as large blue crystals belonging to the triclinic system, and is the salt from which nearly all the other compounds of copper are obtained. Copper sulphate may be prepared by dissolving copper oxide in sulphuric acid, or by heating copper with concentrated sulphuric acid. Considerable quantities of copper sulphate are produced by the oxidation of copper-pyrites when roasted in the air, but always mixed with more or less ferrous sulphate. It cannot be completely freed from this impurity by simple recrystallization, as the two salts crystallize together, but if sufficient nitric acid is added to oxidize the iron to the ferric state, the solution evaporated to dryness, and the dry mass extracted with water, most of the iron remains behind as a basic salt. Copper is precipitated from the blue solution of

cupric sulphate, produced in mines where copper-pyrites is worked, by adding scrap iron. The metal so obtained is known as *cement-copper.*

Cupric sulphate is easily soluble in water; one part of the salt dissolves in 2·5 parts of cold water or in 0·5 part of boiling water. The blue crystals slightly effloresce when exposed to the air, and lose 4 molecules of their water of crystallization at 100°, but the fifth molecule of water (water of constitution) is only expelled at about 200°. The anhydrous salt is white, but regains its blue colour in contact with water, being reconverted into the hydrated compound. The energy with which anhydrous cupric sulphate unites with water is so great that we employ it to abstract the last traces of water from 99 per cent. alcohol, and to remove traces of water from many other liquids in which the salt does not dissolve.

Cupric sulphate unites with the sulphates of the alkalies and forms double salts, which may easily be obtained in the crystalline form combined with 6 molecules of water. They are of a lighter colour than cupric sulphate and less soluble in water.

Cupric Ammonium Sulphates.—If a concentrated aqueous solution of cupric sulphate is mixed with strong ammonia until the precipitate of cupric hydrate which is first produced is redissolved, a deep blue liquid is produced, which, on standing, or better, when covered with a layer of alcohol, deposits a layer of deep blue crystals of the composition: $SO_2 \cdot O_2Cu + 4NH_3 + H_2O$. These crystals gradually decompose and become opaque when exposed to the air, and when heated to 150° lose their water with 2 molecules of ammonia, leaving a green powder of the composition: $SO_2 \cdot O_2Cu + 2NH_3$.

The formation and constitution of these two compounds may be represented as follows (see p. 563). On the addition of ammonia to cupric sulphate, ammonium sulphate and cupric hydrate are first produced, and the latter compound then appears to unite with ammonia and form *cupri-diammonium hydrate*:—

$$Cu\begin{cases}OH\\OH\end{cases} + 2NH_3 = \begin{matrix}OH \cdot NH_3\\OH \cdot NH_3\end{matrix}\Big\}Cu,$$

or the hydrate of a hypothetical diammonium in which 2 atoms of hydrogen are displaced by 1 atom of diad copper. This substance does not appear to exist in the free state, but unites at once with the ammonium sulphate, and produces the blue salt, ***diammon-cupri-diammonium sulphate***, **thus:—**

$$SO_2\begin{cases}ONH_4\\ONH_4\end{cases} + \begin{matrix}OH\cdot NH_3\\OH\cdot NH_3\end{matrix}\Big\}Cu = SO_2\begin{cases}ONH_3\cdot NH_3\\ONH_3\cdot NH_3\end{cases}\Big\}Cu + 2H_2O,$$

Ammonium sulphate — Cupri-diammonium hydrate — Diammon-cupri-diammonium sulphate

which may be considered as ammonium sulphate in which two atoms of hydrogen have been displaced by the diad radical *cupri-diammonium*: $\begin{matrix}NH_3\\NH_3\end{matrix}\Big\}Cu$. On heating the blue compound to 150° it parts with two molecules of ammonia, and leaves the green powder mentioned above, which is *cupri-diammonium sulphate*:—

$$SO_2\begin{cases}ONH_3\cdot NH_3\\ONH_3\cdot NH_3\end{cases}\Big\}Cu = SO_2\begin{cases}ONH_3\\ONH_3\end{cases}\Big\}Cu + 2NH_3.$$

Diammon cupri-diammonium sulphate — Cupri-diammonium sulphate

The constitution of the ammoniacal compounds of cobalt (p. 487) is possibly similar to that of the above salts.

Cupric Nitrate: $(NO_2)_2O_2Cu + 3H_2O$, is easily obtained by dissolving copper in nitric acid, and separates out when the solution is concentrated as dark blue deliquescent crystals, easily soluble both in water and in alcohol.

Cupric Phosphate: $(PO)_2O_6Cu_3 + 3H_2O$, is thrown down as a blue-green precipitate when ordinary sodium phosphate is added to a solution of cupric sulphate. Various phosphates of copper occur in the mineral kingdom.

Cupric Arsenite, probably: $As\begin{cases}O_2Cu\\OH\end{cases}$ is obtained as a green precipitate varying in tint when a solution of sodium arsenite is poured into one of copper sulphate, with constant stirring. This compound is used as a pigment under the name of *Scheele's green*. A second green pigment—known as *Schweinfurt-green*—is a double compound of copper arsenate and acetate. Both these compounds are highly poisonous, and their use is therefore very limited.

Cupric Carbonates.—All the known carbonates of copper are basic compounds. Even when normal copper sulphate is mixed with normal sodium carbonate, the bluish-green gelatinous precipitate, which after a time changes to a bright green powder, consists of a basic carbonate of the composition: $CO\cdot O_2Cu + Cu(OH)_2 =$

$CO\begin{cases}OCuOH\\OCuOH\end{cases}$ The same compound is found in nature, especially in Siberia, as the beautiful mineral, *malachite*, which in its massive form is used for the manufacture of vases, tops of tables, &c.

A second basic carbonate of copper is the dark blue mineral *azurite*, of the composition : $2CO \cdot O_2Cu + Cu(OH)_2$.

Cupric Acetates.—These compounds belong strictly to organic chemistry, but it may be remarked that normal cupric acetate is soluble in water and is deposited from its solution in blue crystals. The basic acetates are insoluble or difficultly soluble in water. One of these, or rather a mixture of several, is the poisonous substance called *verdigris*.

Cupric Chloride : $CuCl_2 + 2H_2O$, is obtained by dissolving cupric oxide in hydrochloric acid, and on concentrating the solution is deposited in small, green, rhombic prisms. When heated the salt loses its water and the anhydrous chloride remains behind as a yellowish-brown powder, which rapidly attracts moisture from the air and deliquesces. When more strongly heated, it is decomposed into cuprous chloride and free chlorine.

Cupric chloride unites with cupric hydrate and forms basic compounds. One of these is the mineral *atacamite*, and has the composition : $CuCl_2 + 3Cu(OH)_2$. These insoluble basic chlorides may be obtained by mixing a solution of cupric chloride with a quantity of caustic soda insufficient to convert all the copper into cupric hydrate.

Cupric Bromide : $CuBr_2$, closely resembles the chloride. *Cupric Iodide*, strange to say, has not been prepared. If potassium iodide is added to a solution of cupric sulphate, a white precipitate of cuprous iodide is produced and iodine is set free.

Cupric Sulphide : CuS, is thrown down as a black precipitate when sulphuretted hydrogen is led through a solution of a cupric salt. In the moist state it readily attracts oxygen from the air and is converted into cupric sulphate, and must therefore be washed with water containing sulphuretted hydrogen and dried in a vacuum. When heated in a stream of hydrogen it parts with one-half of its sulphur and is converted into cuprous sulphide : Cu_2S. Cupric

sulphide is found in nature as the mineral *covellite* in dark-blue hexagonal prisms.

Cuprous Compounds.

Cuprous Oxide: Cu_2O.—This compound is found in nature as the mineral *cuprite* or *red copper ore* either in compact crystalline masses, or else in small regular octahedra. The crystalline compound may be artificially prepared by fusing solid cuprous chloride with dry sodium carbonate. It then remains as a red crystalline powder when the fused mass is afterwards extracted with water. It may also be prepared in the same form but in smaller crystals, by gently warming a solution of cupric sulphate with an excess of caustic soda and grape sugar. The grape sugar is then oxidized by half the oxygen contained in the copper oxide. Cuprous oxide remains unchanged in the air and is quite insoluble in water. When treated with hydrochloric acid, it is converted into white cuprous chloride, which dissolves in excess of the acid, and forms a colourless solution in the absence of air. Dilute sulphuric acid converts it into cupric sulphate with the separation of one-half of the copper as a red powder. Other oxy-acids behave in the same way, except nitric acid, which completely dissolves it.

Cuprous Hydrate: $Cu_2(OH)_2$.—When a solution of cuprous chloride in hydrochloric acid is poured into an excess of caustic soda, cuprous hydrate is thrown down as a yellow crystalline precipitate. The compound is very unstable, rapidly absorbing oxygen from the air, and producing blue cupric hydrate.

The cuprous oxy-salts are very unstable, and are scarcely known. The corresponding compounds with the halogens are, however, more permanent.

Cuprous Chloride: Cu_2Cl_2.—This substance is a white crystalline powder, insoluble in water, but soluble in hydrochloric acid, from which it crystallizes in white tetrahedra. Cuprous chloride may be obtained by boiling cupric chloride with excess of hydrochloric acid and metallic copper in a stream of carbonic acid to exclude the air, the oxygen of which would oxidize the cuprous chloride thus produced. On afterwards pouring the clear acid solution into a large quantity of cold boiled water, the cuprous chloride is deposited as a white crystalline powder. Cuprous chlo-

ride may also be prepared by adding a solution of stannous chloride containing free hydrochloric acid to a solution of cupric chloride. It then crystallizes out also as white tetrahedra, while the stannic chloride, produced at the same time, remains dissolved in the acid liquid.

Cuprous chloride when exposed to the air in the moist state becomes of a green colour, and at 100° large quantities of oxygen are absorbed, forming the oxy-chloride: $CuCl_2,CuO$. But if this compound is further heated (up to about 400°), it again parts with its oxygen and leaves cuprous chloride. By this means, considerable quantities of oxygen may be obtained from the air.

Ammonia, as well as hydrochloric acid, dissolves considerable quantities of cuprous chloride, and both solutions absorb carbonic oxide. The compound which is produced is deposited in colourless scales when a strong solution of cuprous chloride in hydrochloric acid is saturated with the gas. The ammoniacal solution also absorbs and unites with certain gaseous hydrocarbons, especially acetylene.

Cuprous Iodide: Cu_2I_2, is a white powder insoluble in water and dilute acids, and is deposited when potassium iodide is added to a solution of cupric sulphate containing sulphurous acid or ferrous sulphate, these two substances acting as reducing agents. The insolubility of cuprous iodide makes this salt useful for separating iodine from solutions of its salts. Unlike cuprous chloride, the iodide remains unaltered when exposed to the air.

Cuprous Sulphide: Cu_2S, is obtained by heating finely-divided copper with sulphur, or by heating cupric sulphide in a stream of hydrogen. It forms a dark-grey mass, which melts at a red-heat, and when slowly cooled may be obtained in a crystalline form. Cuprous sulphide is found in nature as *copper-glance*, which crystallizes in fine rhombic prisms. It also occurs united with other sulphides—*e.g.* with iron sulphide in *copper-pyrites* and *purple-copper ore*, as well as with the sulphides of silver, antimony, arsenic, &c., in other minerals.

Alloys of Copper.—Few metals are so largely used as copper, both in the form of its salts, and as alloys with other metals. The most important of these alloys are those with zinc, tin, nickel, and silver respectively.

Brass is an alloy of copper and zinc obtained by melting the

two metals together, and is of a darker or lighter colour accordingly as it contains more or less copper. Ordinary brass contains about 70 parts of copper to 30 parts of zinc. A larger proportion of zinc makes an alloy of a pale yellow colour, known as *Muntz-metal*, and largely used for sheathing wooden ships. By increasing the percentage of copper and adding a little tin, a more malleable alloy is obtained, which can be beaten into thin sheets, and is called *tombac* or *Dutch metal.*

Gun-metal, *bronze* and *bell-metal* are all alloys of copper and tin, with about 80 to 90 per cent. of copper, to which a little lead or zinc is often added. Bronze contains less copper than gun-metal, and bell-metal less than bronze. *Speculum-metal* is a hard white alloy of about 1 part of tin and 2 parts of copper, to which some arsenic is not unfrequently added. It takes a high polish, and is used for the mirrors in reflecting telescopes.

An alloy of copper and nickel is used for small coins in Germany, Belgium, and some other countries; in Switzerland the small coins are made of an alloy of copper, nickel, zinc, and silver. German-silver or nickel-silver is an alloy of copper, nickel, and zinc (p. 492). All the silver used in the arts consists of an alloy of copper and silver; and, finally, an alloy of copper and aluminium, containing about 9 parts of the former metal to 1 part of the latter, forms *aluminium-bronze* or *aluminium-gold*, a tenacious, bright yellow alloy, largely used in the manufacture of small articles.

Detection of Copper Compounds.

Copper belongs to those metals of which the sulphides are insoluble in dilute acids, and are separated when a stream of sulphuretted hydrogen is led through an acid solution of one of their salts. The cupric sulphide then obtained is black and resembles lead, bismuth, and some other sulphides. This precipitation of cupric sulphide from acid solutions serves to distinguish copper from nickel, which it otherwise resembles in some points. A characteristic test for a solution of a copper salt is the bluish precipitate produced on the addition of ammonia and the dark blue solution obtained when the ammonia is added in excess. A solution of a copper salt, even when extremely dilute, gives, on the addition of potassium ferrocyanide, a reddish brown precipitate of cupric ferrocyanide: Cu_2FeCy_6; only uranium compounds form a precipitate of this colour with potassium ferrocyanide

Small quantities of a compound of copper may be easily detected by heating with borax on a platinum wire before the blowpipe. A green bead is then formed when heated in the outer flame, which becomes colourless or of a dirty red colour (from cuprous oxide) in the reducing flame. The red cuprous oxide may be more readily obtained by the addition of a trace of stannic oxide, or any compound of tin, and then heating in the reducing flame.

NOBLE METALS.

THIS group includes mercury, silver, gold, platinum, and five other rare metals allied to platinum; they have been called *noble* because they do not tarnish in the air at the ordinary temperature. They are further distinguished by the fact that their oxides are all decomposed when heated into the metal and free oxygen, with the exception of those of osmium and ruthenium, which volatilize unchanged.

MERCURY.

Chemical Symbol: Hg.—*Atomic Weight*: 200.

This metal, with the exception of gallium, is the only one which is liquid at the ordinary temperature, and as it possesses a white colour like silver, is sometimes called *quicksilver*. It is only sparsely distributed in nature, but large quantities are found in the few localities where it occurs. Mercury is sometimes found free in the mineral kingdom or alloyed with silver or gold, but far more commonly in combination with sulphur as *cinnabar*: HgS. The mercury mines of Idria in Austria and of Almaden in Spain have been worked for centuries, and considerable quantities of the metal are also obtained from China. In late years large deposits of cinnabar have been discovered in California.

To extract mercury from cinnabar on a small scale the powdered ore is mixed with quicklime and heated in a retort, the neck of which dips under water. During the heating calcium sulphide and mercuric oxide are formed, and the latter compound then breaks up into mercury and oxygen. The mercury then condenses under the water, and the oxygen partly escapes, but principally serves to convert the calcium sulphide into calcium sulphate.

On the large scale mercury is obtained from cinnabar by roasting the ore with excess of air in specially constructed furnaces

and passing the vapours of sulphurous anhydride and mercury which are thus produced through a series of chambers or through rows of earthenware vessels, where the mercury condenses.

Commercial mercury, even when it has been distilled, is never pure, but contains mechanical impurities as well as traces of zinc, lead, and other less volatile metals dissolved in it. The presence of these impurities may be easily detected by allowing a drop of the metal to flow over the hand, when it runs off clear if pure, but leaves a dirty, dull *tail* on the skin when contaminated with other metals. Mechanical impurities may be separated by filtering the mercury through a filter of writing-paper with a pin-hole at the base. To separate the dissolved metals the mercury is placed in a flat dish and covered with a layer of ordinary nitric acid. The acid then oxidizes some of the mercury and produces mercurous nitrate, which then transfers part of its oxygen to the metals mixed with the mercury. After the whole has stood for several days, with frequent stirring, the acid liquid is poured off, the metal washed with water, then run through a separating-funnel and dried. This method separates most of the impurities contained in the metal, but chemically pure mercury can only be obtained by other and more tedious processes.

Mercury has a specific gravity of 13·6: it solidifies at $-40°$ to a crystalline malleable mass, with a specific gravity of 14·4. Although the metal only boils at 357°, it volatilizes even at the ordinary temperature of the air; if a piece of gold leaf is suspended in a jar containing a little mercury, it combines with the mercury vapour and a white amalgam is formed on its surface.

Mercury remains unchanged in the air at the ordinary temperature, but when heated to about 300° it combines with oxygen and becomes changed into red mercuric oxide, which coats the metal. It is completely insoluble in water and is not attacked by hydrochloric or dilute sulphuric acid. Concentrated sulphuric acid is also without action upon it at the ordinary temperature, but when heated dissolves it, producing mercuric sulphate and sulphurous anhydride. The best solvent for mercury is nitric acid, with which it forms either mercuric or mercurous nitrate according to different conditions.

The vapours of metallic mercury and mercury compounds, especially those soluble in water, are all poisonous. Even the lower animals cannot exist in an atmosphere containing traces of mercury vapour. Entomological collections may be effectually

preserved from destruction by minute animals if a few drops of mercury are placed in the cases containing the specimens.

Compounds of Mercury.

Mercury, like copper, forms two series of compounds—the one containing a single atom of the diad metal, and the other containing two atoms of mercury, which also perform the functions of a diad. (See App.) These two series of compounds are the *mercuric* and *mercurous* compounds respectively. Many are highly valued and powerful medicines.

Mercuric Compounds.

Mercuric Oxide: HgO.—If mercury is heated in the air to about 300°, it gradually becomes oxidized and converted into a red powder of mercuric oxide (p. 10). This change goes on too slowly to prepare any quantity of the oxide, and it is preferable to obtain it from its nitrate. For this purpose dry mercuric nitrate is mixed with an equal weight of mercury, and the mixture gently heated as long as acid vapours are given off. The oxide then remains as a heavy, red, crystalline powder, of specific gravity 11·2, and which becomes of a paler colour when rubbed.

Besides this crystalline form of mercuric oxide, a second modification may be obtained as an amorphous yellow powder, by precipitating a solution of mercuric nitrate with caustic soda. Mercury, like the other noble metals, is precipitated from its solutions by the alkalies and other strong bases as the oxide and not as the hydrate. Mercuric hydrate is unknown.

Mercuric oxide, as previously stated (p. 10), breaks up into mercury and oxygen when heated.

Mercuric Sulphate: $SO_2 \cdot O_2Hg$, is obtained by dissolving mercuric oxide or metallic mercury in sulphuric acid, in the latter case with evolution of sulphurous anhydride. It unites with a small quantity of water to form a colourless crystalline compound containing 1 molecule of water. With a large quantity of water it is decomposed into free sulphuric acid and a basic sulphate of the composition: $SO_2 \cdot O_2Hg + 2HgO$, which separates as a heavy lemon-coloured powder. This compound was formerly used in medicine under the name of *turpeth mineral*. Mercuric sulphate

is manufactured on a large scale, and used for the preparation of the two chlorides of mercury.

Mercuric Nitrate: $(NO_2)_2O_2Hg + 8H_2O$, may be prepared by acting on mercury with an excess of nitric acid, until a drop of the solution no longer gives a precipitate with hydrochloric acid—a proof that it contains no mercurous nitrate. The acid solution, when sufficiently concentrated, and when cooled to $-15°$, deposits large, colourless, rhombic crystals of the above composition. This salt is unstable; it melts in its water of crystallization at 7°, and changes into a basic salt of the composition: $(NO_2)_2O_2Hg + HgO + 2H_2O$, which is also deposited when a hot concentrated solution of mercuric nitrate is allowed to cool. Both these salts are decomposed by water, yielding a still more basic compound: $(NO_2)_2O_2Hg + 2HgO + H_2O$, which separates as yellow crystals insoluble in water. When any of these compounds are gently heated, brown nitrous fumes are evolved and red mercuric oxide remains behind.

Mercuric Chromate is thrown down as a brick-red precipitate when potassium chromate is added to a solution of mercuric nitrate.

Mercuric Chloride: $HgCl_2$.—This important salt, which is commonly called *corrosive sublimate*, crystallizes from its aqueous solution in colourless needles of specific gravity 5·4. It melts to a clear liquid at 288°, boils at about 300°, and can be sublimed unchanged. The salt requires 14 parts of cold water for solution, but less than 2 parts of boiling water. It is more easily soluble in alcohol and in ether.

Mercuric chloride may be obtained by dissolving the metal in aqua regia, when it crystallizes from the concentrated acid solution. It is, however, more commonly prepared in the dry way by sublimation. For this purpose a mixture of common salt and mercuric sulphate is heated in a glass retort or flask, on a sand-bath, when the mercuric chloride thus produced condenses in the upper and cooler parts of the vessel as a crystalline cake, which is removed by breaking open the vessel when cold. The operation must be carried on under a good draught on account of the poisonous nature of the vapours of the chloride, some of which always escape into the air. The following reaction represents the process:—

$$SO_2 \cdot O_2Hg + 2NaCl = HgCl_2 + SO_2(ONa)_2.$$

Mercuric chloride readily parts with one-half of its chlorine when heated with substances which easily combine with this element, and is converted into mercurous chloride. Thus, an intimate mixture of arsenic and mercuric chloride gives arsenious chloride when heated (p. 247).

Corrosive sublimate is an important medicine, but extremely poisonous, and can therefore only be given in small doses ($\frac{1}{16}$ to $\frac{1}{8}$ grain, or 4 to 8 milligrammes). Its solution coagulates albumen, and possesses powerful antiseptic properties. Wood which has been impregnated with a solution of corrosive sublimate is protected both from decay and from the attacks of insects. It has been proposed to saturate the wood of wooden bedsteads with its solution, but the process is not to be recommended on account of the poisonous nature of the dust given off by the dry wood.

Caustic soda when added to a solution of mercuric chloride gives a yellow precipitate of mercuric oxide, but ammonia when added to the same solution behaves differently, and produces a white precipitate of the composition: $\left.\begin{matrix}NH_2Cl\\NH_2Cl\end{matrix}\right\}Hg_2$, which is to be considered as a diammonium dichloride, in which one-half of the hydrogen (4 atoms) has been displaced by mercury (2 atoms), and is, therefore, *dimercuri-diammonium chloride.* This substance is used in medicine under the name of *infusible white precipitate.*

If a mixture of mercuric and ammonium chlorides is precipitated with sodium carbonate, a similar white compound is obtained of varying composition, and which melts, when heated, to a yellowish liquid. This substance is called *fusible white precipitate.*

When a solution of mercuric chloride is gradually added to a boiling mixture of ammonium chloride and ammonia, so that the precipitate which is produced redissolves, the solution deposits on cooling colourless rhombohedra of the composition: $\left.\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}\right\}Hg$ —*i.e. mercuri-diammonium chloride.* This compound is closely related to the infusible white precipitate, from which it may be obtained by boiling with ammonium chloride:—

$$\left.\begin{matrix}NH_2Cl\\NH_2Cl\end{matrix}\right\}Hg_2 \quad + \quad 2NH_4Cl \quad = \quad 2\left.\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}\right\}Hg.$$

Mercuric Bromide: $HgBr_2$, resembles the chloride, but is more difficultly soluble in water.

Mercuric Iodide : HgI_2.—When solutions of mercuric chloride and potassium iodide are mixed, a yellow precipitate of mercuric iodide is first produced, which soon turns red, and is soluble either in excess of mercuric chloride or of potassium iodide. On cooling its warm saturated solution in potassium iodide or in alcohol, the salt crystallizes in fine red tetragonal pyramids. It is insoluble in water. When heated the salt becomes yellow, then melts and sublimes in bright yellow crystals belonging to the rhombic system. This yellow modification of mercuric iodide readily passes into the red form; mere contact with the point of a needle is sufficient to convert an entire quantity of the yellow crystals into the other modification.

A solution of mercuri[illegible] [illegible] assium iodide, and made alkaline by caustic pot[illegible] the detection of minute quantities of ammonia or [illegible] salts, and is called *Nessler's solution* (p. 387).

Mercuric Cyanide : $HgCy_2$.—Red mercuric oxide readily dissolves when digested with dilute hydrocyanic acid, and mercuric cyanide crystallizes from the clear solution in brilliant colourless quadratic prisms. The crystals contain much enclosed water, but none combined as water of crystallization; the substance is extremely poisonous. Mercuric cyanide is decomposed on heating into mercury and cyanogen, a portion of the latter gas taking the form of brown paracyanogen (p. 311). If on digesting mercuric oxide with hydrocyanic acid the oxide is in excess, an alkaline solution is obtained, from which crystals of a basic cyanide: $HgCy_2 + HgO$, may be separated.

Mercuric Sulphide, *Cinnabar* : HgS.—This compound, distinguished by its beautiful red colour, is the commonest form in which mercury occurs in nature, and is the substance exclusively used for the extraction of the metal.

The mineral cinnabar is sometimes found in small, transparent, red crystals, belonging to the hexagonal system, but generally occurs in compact dark-red masses. It volatilizes unchanged when heated, and in this respect differs from the corresponding red oxide. Cinnabar may be obtained artificially by rubbing together a mixture of 25 parts of mercury with 4 parts of flowers of sulphur. This first produces an amorphous black sulphide, which when heated

in a suitable vessel yields a sublimate of cinnabar as a translucent, red crystalline mass of fibrous structure.

Mercuric sulphide is produced in the wet way by leading sulphuretted hydrogen into a solution of a mercuric salt. A black precipitate is then produced, which has the same composition as cinnabar and into which it may be converted by sublimation. When the sulphuretted hydrogen is led into the mercuric salt a white precipitate is first thrown down, which soon becomes yellow, then red, and finally black. These intermediate substances are double compounds, in varying proportions, of mercuric sulphide and the mercuric compound used for the precipitation.

Mercuric sulphide is insoluble both in nitric acid and in hydrochloric acid, and only dissolves in aqua regia. This property enables us to separate it from the sulphides of other metals —*e.g.* copper—which dissolve in nitric acid. The sulphide in the form of powdered cinnabar is the valuable pigment *vermilion*, which is prepared either by grinding sublimed cinnabar or by various wet processes. The colour is improved by continued rubbing or by allowing the powder to stand for some time in contact with a solution of potassium pentasulphide at a temperature of 50°.

Mercurous Compounds.

Mercurous Oxide : Hg_2O.—This compound is much less stable than mercuric oxide; it may be obtained as a black amorphous precipitate by mixing a solution of mercurous nitrate with a slight excess of caustic soda. When rubbed, or when heated to 100°, it decomposes into mercuric oxide and free mercury. The same change is also produced by the action of light, and it must, therefore, be filtered, washed, and dried in the dark. Undecomposed mercurous oxide dissolves completely in dilute nitric acid.

Mercurous Nitrate: $(NO_2)_2O_2Hg_2 + 2H_2O$.—If mercury is covered with a layer of moderately dilute nitric acid and allowed to stand for some time at the ordinary temperature, colourless transparent crystals gradually separate out in the form of rhombic plates. This salt is mercurous nitrate. The crystals easily dissolve in the mother-liquor when warmed, and reseparate when the solution again cools. The salt is decomposed by water, with the separation of a yellow basic salt: $(NO_2)_2O_2Hg_2 + Hg_2O + H_2O$.

A second basic salt, containing less mercurous oxide, is obtained by warming nitric acid with excess of mercury; it crystallizes from its hot saturated solution in transparent colourless prisms.

On the addition of ammonia to a solution of mercurous nitrate a black precipitate, resembling mercurous oxide, is obtained. This substance contains, however, the elements of ammonia and has a varying composition; its chief constituent is probably a compound of the composition: $\left.\begin{matrix} NO_2 \cdot ONH_2 \\ NO_2 \cdot ONH_2 \end{matrix}\right\} Hg_4$—*dimercuroso-diammonium nitrate*—*i.e.* diammonium nitrate in which four atoms of hydrogen are displaced by four monad atoms of mercury. It was formerly used in medicine under the name of *Mercurius solubilis Hahnemanni.*

Mercurous Chromate: $CrO_2 \cdot O_2Hg_2$, is thrown down as a red precipitate on adding a solution of potassium chromate or dichromate to one of mercurous nitrate; it is quite insoluble in water, and is used for the separation and quantitative estimation of chromic acid. The dry salt decomposes when heated into mercury and oxygen, which are given off, and green chromic oxide, which remains behind. From the weight of chromic oxide so obtained that of the chromic acid precipitated may be easily calculated.

Mercurous Chloride, *Calomel*: Hg_2Cl_2.—This salt, which like corrosive sublimate is a valuable medicine, is distinguished by its complete insolubility in water. It is found in nature as the mineral *horn-quicksilver*, and may be prepared artificially either in the wet way (by precipitation) or in the dry way (by sublimation). By the former method, it is obtained as a white curdy precipitate, when hydrochloric acid or a soluble chloride is added to a solution of mercurous nitrate. This precipitate when washed and dried forms a heavy white powder. Calomel is also obtained in the dry way when a mixture of mercuric chloride and mercury is heated. In grinding the two substances together it is well to add a little alcohol to prevent the formation of any dust of the poisonous mercuric chloride. Thin glass flasks are then about one-third filled with this mixture, and heated on a sand-bath; vapours of mercury and mercuric chloride are thus formed, and unite together to produce mercurous chloride, which sublimes and condenses in the upper and cooler parts of the flasks. The operation must be conducted under a hood with a good draught on account of the

extremely poisonous nature of the vapours of mercuric chloride, some of which always escape from the flasks.

This process is not, however, used for the manufacture of calomel, but a mixture of mercuric sulphate and common salt (which yields mercuric chloride when heated) is ground up with an equal quantity of mercury to that already contained in the sulphate, and then heated in glass or earthenware vessels. Mercurous chloride then sublimes and sodium sulphate remains behind.

Calomel prepared in either of these ways always contains more or less corrosive sublimate, which may be extracted from it by digesting the powdered substance with warm alcohol. This purification is especially necessary if the calomel is to be employed for medicinal purposes. Calomel is much less poisonous than corrosive sublimate, and can therefore be given in larger doses.

Mercurous chloride when treated with ammonia becomes converted into a black powder of the composition: $\left.\begin{matrix} NH_2Cl \\ NH_2Cl \end{matrix}\right\} Hg_4$—*di-mercuroso-diammonium chloride*, and in this way may be distinguished from silver chloride, which dissolves in ammonia.

Mercurous Bromide: Hg_2Br_2, closely resembles the chloride in its properties.

Mercurous Iodide: Hg_2I_2, is thrown down as a dirty green precipitate when a solution of potassium iodide is mixed with one of mercurous nitrate: it may also be obtained by rubbing together mercury and iodine in the correct proportions. The compound turns black in the light, and when heated is decomposed into mercuric iodide and mercury.

Mercurous Cyanide has not yet been prepared.

Mercurous Sulphide: Hg_2S, is possibly produced when sulphuretted hydrogen is led into a solution of mercurous nitrate; it is, however, very unstable, and soon decomposes into mercuric sulphide and mercury.

Amalgams.

Mercury readily unites with most metals, and produces alloys —generally known as amalgams. Often mere contact at the ordinary temperature suffices to produce an amalgam, as in the case of silver, gold, and the alkali metals. Most amalgams may be

obtained in the solid crystalline form, and are all soluble in excess of mercury. An amalgam of iron can only be obtained with difficulty, and iron vessels are therefore employed to contain the metal.

Sodium amalgam may be easily obtained as a solid crystalline mass by adding 4 parts of sodium, in small quantities at a time, to 100 parts of warm mercury contained in a mortar. As each small piece of sodium is pressed under the mercury with the pestle, the two metals unite with a hissing noise, and a sufficient evolution of heat to volatilize some of the mercury. The amalgam remains liquid as long as it is warm, but becomes a crystalline solid when cold. Mercury unites still more energetically with potassium.

A piece of gold when dipped into mercury becomes at once covered with a white layer of gold amalgam, and soon completely dissolves. Silver also easily dissolves in an excess of mercury. The readiness with which these two metals unite with mercury is utilized to separate them from their ores. These ores when shaken with mercury yield amalgams, from which the mercury can be afterwards distilled, leaving silver or gold behind (amalgamation process). One of the most useful amalgams is that of tin, which is used for silvering ordinary looking-glasses (p. 522).

Metallic mercury is used for a number of technical and scientific purposes—for example, in the construction of barometers and thermometers, and for the mercury air-pump (Sprengel's pump). It is also used in the laboratory to collect gases which are dissolved by water but which do not act upon mercury—*e.g.* ammonia, hydrochloric acid. Chlorine cannot be collected over mercury, as the two substances at once unite with one another and produce a chloride.

Detection of Mercury Compounds.

All solid compounds of mercury when mixed with quick-lime or dry sodium carbonate and heated in a small tube are decomposed and yield metallic mercury, which condenses in the cooler parts of the tube in minute glistening globules.

Soluble mercuric salts may be recognized by the yellow precipitate of mercuric oxide produced by caustic soda and the white precipitate formed on the addition of ammonia. Black mercuric sulphide, which is produced when a stream of sulphuretted hydrogen is passed through a solution of a mercuric salt, is distinguished from other black sulphides produced in the same way (*e.g.* th

of copper, lead, bismuth) by remaining unchanged when warmed with nitric acid. The soluble mercurous salts, of which only one or two are known, give a white precipitate of mercurous chloride with hydrochloric acid, which blackens on the addition of ammonia. Caustic soda and ammonia, as well as ammonium or sodium carbonate, all produce black precipitates with a solution of mercurous nitrate. If a solution of stannous chloride is added to a solution of a mercuric or mercurous salt, a white precipitate of mercurous chloride is produced in both cases, in the former with the simultaneous production of stannic chloride. And if this precipitate of mercurous chloride is mixed with a further quantity of stannous chloride and some hydrochloric acid, it is reduced to a grey powder of metallic mercury, the particles of which unite when boiled and produce small globules of the metal.

SILVER.

Chemical Symbol: Ag.—*Atomic Weight*: 108.

Silver is tolerably widely distributed in nature, but is seldom found in large quantities. It occurs as *native silver* crystallized in regular octahedra, and united with chlorine as *horn-silver* ($AgCl$), as well as with the other halogens bromine and iodine, or even with all three together: it is also occasionally found mixed with mercury as *amalgam*. More important than these are the compounds of silver with sulphur, *silver-glance* (Ag_2S), and those containing silver sulphide united with other sulphides (*e.g.* those of arsenic, antimony, and copper). These double sulphides form the minerals *dark-red silver ore* or *pyrargyrite* ($3Ag_2S,Sb_2S_3$), *light-red silver ore* or *proustite* ($3Ag_2S,As_2S_3$), and *silver copper-glance* (Ag_2S,Cu_2S).

A considerable quantity of silver is extracted from argentiferous lead by the process of cupellation, which has been already described under lead (p. 500). From ores containing little lead the silver is extracted by the process of *amalgamation*, which varies in different countries according to the nature of the ore and according as fuel is cheap or dear. The rich ores of Nevada and Colorado in the United States are roasted with common salt, by which the silver loses its sulphur and is converted into silver chloride. The roasted ores are then mixed with water and scrap iron and rotated

in barrels for some time, when the iron gradually reduces the silver to the metallic state. As soon as this change has been produced, mercury is introduced into the barrels, and the silver amalgam so obtained run off, dried, and distilled. Mercury then passes over into a condenser and metallic silver remains behind. In Mexico and Chili, where fuel is scarce and dear, the silver is converted into chloride by a mechanical process which consists in mixing the ground ore with common salt and salts of copper and iron by the treading of mules; mercury in excess is next added, part of which reduces the silver chloride with formation of calomel, the remainder forming an amalgam which is afterwards distilled. Various wet processes are also used for the extraction of silver from very poor ores.

Pure silver may be obtained by precipitating a solution of a silver salt with hydrochloric acid, and fusing the pure dry silver chloride so produced with dry sodium carbonate in an unglazed porcelain crucible. When cold, the silver is found at the bottom of the crucible covered with a layer of fused sodium chloride.

Silver is a white, lustrous metal, with a specific gravity of 10·6. It is soft, and so malleable that it can be beaten out into extremely thin leaves (silver leaf). Silver melts at a lower temperature than copper, and although it does not oxidize in the air, possesses the property of dissolving oxygen when in the liquid state. This oxygen, which is only dissolved in the silver, not chemically combined with it, is again given off when the silver solidifies, producing the phenomenon known as the *spitting* of silver. Pure silver is said to absorb as much as 22 times its volume of oxygen. The property is only possessed by the pure metal: the addition of a small quantity of lead prevents the absorption of the gas and the subsequent spitting.

Silver combines far more readily with sulphur than with oxygen. Sulphuretted hydrogen is decomposed by silver, and the metal becomes covered with a thin brown or black layer of silver sulphide. Hydrochloric acid does not attack the metal, but it is readily dissolved by nitric acid with evolution of brown nitrous fumes, and formation of silver nitrate. Concentrated sulphuric acid dissolves silver in the same way as copper and mercury, producing silver sulphate and sulphurous anhydride. Silver is precipitated from solutions of its salts by other more positive metals—*e.g.* zinc, iron, and copper—and also by certain reducing substances, such as ammonium sulphite, grape sugar, aldehyde, and tartaric acid.

Some of these substances cause a deposit of the silver as a uniform coating on the walls of the vessel used for the experiment, and produce a mirror of metallic silver.

All commercial silver, including silver coins, always contains from 5 to 10 per cent of cópper. To prepare pure silver from this alloy, the metal may be dissolved in nitric acid, the solution filtered from a trace of gold which remains behind as a black powder, and the filtrate precipitated with hydrochloric acid or a solution of common salt. The silver chloride is then washed, dried, mixed with dry sodium carbonate, and heated in an unglazed crucible. Sodium chloride and silver carbonate are then produced, and the latter compound is decomposed at a red-heat into carbonic acid, oxygen, and silver. After cooling, a button of pure silver is found at the bottom of the crucible covered with a layer of fused sodium chloride.

Compounds of Silver.

Silver is one of the few metals which exists as a monad element in nearly all its compounds. In this respect it resembles the alkali metals and thallium, and like sodium it also forms a peroxide, containing the metal as a diad. Its sulphate unites with aluminium sulphate when heated in sealed tubes, and produces silver alum, isomorphous with the alums of potassium and thallium.

Silver Oxide: Ag_2O, is precipitated as a brown amorphous powder when silver nitrate is mixed with pure caustic soda or some other soluble base. As ordinary caustic soda always contains sodium chloride, the silver oxide obtained by it is mixed with silver chloride, and it is therefore preferable to use baryta-water. Silver oxide is not quite insoluble in water; it imparts a metallic taste and a faint alkaline reaction to it. When exposed to the light it slowly decomposes at the ordinary temperature into silver and oxygen—a change which takes place rapidly when the compound is heated. Hydrogen reduces it completely even at 100°. Silver oxide unites readily with all acids, but few of its salts are soluble.

If freshly precipitated silver oxide is digested with strong ammonia it is converted into a black powder, which may also be obtained by adding caustic potash to an ammoniacal solution of silver nitrate. This substance is one of the most unstable compounds known; it explodes violently when slightly pressed, even

when moist. It is known as *Berthollet's fulminating silver*, but we are quite ignorant of its composition. Possibly it is silver amide: NH_2Ag, or silver nitride: NAg_3.

Silver Peroxide: AgO or Ag_2O_2.—This little-studied compound is obtained in the form of black shining octahedra when ozone acts on a moist silver plate, or when an electric current is passed through a strong solution of silver nitrate. It is then deposited on the positive pole, for which it is best to employ a stout platinum wire. The compound is less stable than silver oxide; it decomposes when heated over 100° into silver oxide and oxygen, and when inflammable substances, such as sulphur or phosphorus, are brought into contact with it, they are oxidized with an explosion. When warmed with nitric acid it produces silver nitrate, and oxygen is evolved. Cold nitric acid dissolves it and produces a brown liquid.

Silver Sulphate: $SO_2(OAg)_2$.—When silver is warmed with concentrated sulphuric acid, the metal gradually dissolves, with evolution of sulphurous acid, and silver sulphate is deposited as small glistening crystals. The salt is difficultly soluble in water, and may therefore be prepared by adding a solution of sodium sulphate to one of silver nitrate. As the salt is far more soluble in hot than in cold water, it is deposited when the above solutions are made hot, mixed, and the mixture allowed to cool. It crystallizes in small rhombic prisms, which are isomorphous with anhydrous sodium sulphate. At a low red-heat, silver sulphate melts unchanged, but at higher temperatures it is decomposed into silver, sulphurous and sulphuric anhydrides, and oxygen.

Silver Nitrate: $NO_2 \cdot OAg$.—This, the most important salt of silver, is obtained by dissolving pure silver in nitric acid and evaporating down the acid liquid. It crystallizes in large colourless rhombic plates, is easily soluble in water, and the solution reacts neutral. Alcohol also dissolves considerable quantities of the salt. Silver nitrate melts at about 220°, and solidifies on cooling to a crystalline mass. At a higher temperature it is converted into silver nitrite, which when more strongly heated is completely decomposed, metallic silver remaining behind.

If silver nitrate is carefully melted at the lowest possible temperature and poured into moulds, similar to those used for caustic potash (p. 348), it is obtained in the form of white solid

sticks, which are used as a caustic in surgery under the name of *lunar caustic.* Silver nitrate destroys those bodies which cause the putrefaction and decomposition of organic substances, and also coagulates albumen; hence the spots touched with the caustic become covered with a hard crust of coagulated albumen and fibrin, which soon blackens, especially when exposed to the light. The blackening is due to finely divided metallic silver reduced from the nitrate by the organic matter. A solution of silver nitrate also blackens when exposed to the light in contact with organic substances, and such a solution mixed with gum water is used for marking linen and cotton articles. Characters written with this *marking-ink* gradually blacken when warmed or when exposed to light, and the reduced silver adheres so firmly to the fibres of the stuff, that it is not removed by washing with soap and soda. Such marks may, however, be obliterated by moistening them with a solution of potassium cyanide and then very carefully washing with water, *on account of the extremely poisonous character of this compound.* Potassium cyanide dissolves finely divided silver in the presence of water, producing soluble potassium-silver cyanide with some caustic potash, and free hydrogen :—

$$2KCy + Ag + H_2O = KCy,AgCy + KOH + H.$$

Silver nitrate has many applications in the arts. Large quantities are used in photography for the production of the halogen compounds of silver which are readily decomposed by light.

Silver Phosphate : $PO(OAg)_3$, is produced as a bright yellow precipitate by mixing a solution of common (monacid) sodium phosphate with one of silver nitrate :—

$$PO(ONa)_2(OH) + 3NO_2{\cdot}OAg = PO(OAg)_3 + 2NO_2ONa + NO_2{\cdot}OH.$$

The filtered solution then reacts acid from free nitric acid, and contains some silver dissolved as acid silver phosphate.

Silver Arsenite : $As(OAg)_3$, closely resembles the yellow phosphate. *Silver Arsenate* : $AsO(OAg)_3$, is a reddish-brown powder, and, like the phosphate and arsenite, easily dissolves in nitric acid.

Silver Carbonate : $CO(OAg)_2$, is thrown down on mixing a solution of silver nitrate with one of sodium carbonate as a yellowish-white precipitate, which quickly darkens in the light.

The dry salt loses its carbonic acid at a temperature slightly above 100°.

Silver Chromate: $CrO_2(OAg)_2$, is a dark-red precipitate obtained by mixing solutions of potassium chromate and silver nitrate.

Silver Chloride, Bromide, and Iodide.

These three halogen compounds of silver closely resemble one another, especially in their chemical properties. They all occur in nature, and often associated with one another. They are obtained as curdy precipitates of a white or pale yellow colour, and insoluble in dilute acids when the corresponding halogen acid or haloid salt is added to a solution of silver nitrate. Silver chloride is of a pure white colour, the bromide is faintly yellow, and the iodide has a more decided yellow tint. They all melt when heated without decomposition, and are reduced to the metallic state by zinc when this metal is dipped into one of the fused salts or when zinc is added to the salt suspended in water containing hydrochloric acid. All three dissolve easily in an aqueous solution of sodium thiosulphate or of potassium cyanide, but are distinguished from one another by their solubility in ammonia. *Silver Chloride*: AgCl, when freshly precipitated, easily dissolves in a small quantity of ammonia; *Silver Bromide*: AgBr dissolves only with difficulty and requires a large quantity of the reagent; while *Silver Iodide*: AgI, is almost insoluble in ammonia, but is dissolved by potassium iodide, forming a soluble double salt of the composition: KI,AgI, which crystallizes out when the solution is evaporated down. Silver is scarcely attacked by hydrochloric or hydrobromic acid, but strong hydriodic acid easily converts the metal into silver iodide with evolution of hydrogen.

Silver bromide and iodide are less stable compounds than silver chloride. Both the former are decomposed when heated in a stream of chlorine; silver chloride is then produced, with separation of bromine or iodine respectively. But if a mixed solution of potassium iodide and chloride is added to a small quantity of silver nitrate, the compound first produced is not silver chloride but silver iodide. In the same manner, silver chloride is completely decomposed into silver bromide when boiled with a solution of potassium bromide, and both silver chloride and bromide become converted into silver iodide when treated with potassium iodide. From these results it

has sometimes been imagined that the affinity of silver for chlorine in an aqueous solution is less than for bromine; but if we consider the three equations which represent these changes:—

$$AgCl + KBr = AgBr + KCl$$
$$AgBr + KI = AgI + KBr$$
$$AgCl + KI = AgI + KCl$$

we see that potassium chloride is formed in the first and third equations and potassium bromide in the second, and potassium chloride is a much more stable compound than either the iodide or the bromide, while the bromide is more stable than the iodide. The cause of the reactions is therefore due not to a stronger affinity of silver for bromine or iodine than for chlorine, but to a stronger affinity of potassium for chlorine than for bromine and iodine, and for bromine than for iodine.

The sensibility of the halogen compounds of silver to light, under the influence of which, in the presence of reducing agents, they are reduced to sub-salts and then to metallic silver, makes them very suitable for the production of photographs. The compounds, usually silver bromide or iodide, are suspended in some suitable medium (collodion or gelatine), and glass plates coated with the mixture. These plates are then exposed in the camera to the light reflected from the object of which a picture is required, when the silver iodide or bromide is more or less reduced according to the intensity of the light falling upon it, and according to the length of time which the plate is exposed. On removing the plate from the camera no change can be seen, and no metallic silver has yet been produced: the light has only formed a sub-bromide or iodide without any change of colour. (See App.) But if the exposed plate is brought into a solution of some reducing substance, such as pyrogallic acid or ferrous oxalate, the reducing action which the light has begun is carried further and the sub-bromide or -iodide is now converted into black metallic silver. This process is called *developing*. In order to preserve this picture and to prevent the undecomposed silver salt from blackening when exposed to the light, it must now be *fixed*—a process which consists in dissolving out the undecomposed bromide or iodide by a solution of sodium thiosulphate or potassium cyanide. The picture so obtained shows the bright parts of the object dark and the dark parts light, and is called a *negative*; an ordinary photograph on paper is obtained from this by placing the glass negative over a sheet of paper con-

taining silver chloride in its pores and then exposing to the light. The *print* so obtained is then treated with various solutions containing gold, to make the colour more pleasing, and finally *fixed* with sodium thiosulphate. Not only does the intensity of the light influence its reducing action on the halogen compounds, but light of different colour produces very different effects. Thus the blue and violet parts of the spectrum have a far more powerful reducing action than the green, yellow, and red; and the invisible rays which lie beyond the visible violet (the ultra-violet or actinic rays) act most powerfully of all. Hence all photographic processes must be conducted in a room which is only illuminated with yellow or red light.

Silver Fluoride: AgF, is distinguished from the other halogen compounds of silver by its solubility in water. It may be easily obtained by dissolving silver carbonate in hydrofluoric acid, and crystallizes from its aqueous solution with two molecules of water.

Silver Cyanide: AgCy, is a white curdy precipitate produced by carefully adding a solution of potassium cyanide to silver nitrate. It is insoluble in water and dilute acids, but easily dissolves in ammonia. An excess of potassium cyanide also dissolves it, and produces a soluble double cyanide of the composition: KCy,AgCy, which may be easily obtained in the crystalline form. Unlike the chloride, bromide, and iodide, it is decomposed when heated, yielding cyanogen gas. The grey substance which then remains behind is a mixture of metallic silver and paracyanogen. The soluble compound: KCy,AgCy, is largely used in silver plating. The silver which is deposited at the negative pole when an electric current is passed through a solution of this double cyanide has a more compact form, and adheres more firmly to the substance to be plated than that deposited in a similar manner from any other solution of silver.

Silver Sulphide: Ag_2S.—Silver possesses a strong affinity for sulphur, and even decomposes sulphuretted hydrogen in the presence of air, but remains unchanged in the pure dry gas. The compound may be obtained by melting silver and sulphur together, or by precipitating a salt of silver with sulphuretted hydrogen. When prepared by the latter method it is a black powder easily soluble in nitric acid. Silver sulphide occurs in the mineral kingdom as

silver-glance, and in combination with the sulphides of arsenic or antimony as light and dark red silver ore respectively.

Alloys of Silver.

The numerous articles which are made of silver do not consist of the pure metal, but of an alloy of copper and silver. The pure metal is too soft for ordinary use and would wear away rapidly. But the addition of a few parts per cent. of copper considerably increases it in hardness and makes it more suitable for ordinary purposes. The two metals fuse together in all proportions, and those alloys which only contain 20 per cent. of silver have a reddish colour, while those containing 80 to 90 per cent. are white. English silver coins contain 92·5 per cent. of silver and 7·5 per cent. of copper, while the silver coinage of France, Germany, and Austria, consists of an alloy of 90 parts of silver with 10 parts of copper. The percentage of silver contained in a given alloy is usually expressed in parts per thousand or per *mille*. Thus the *fineness* of the silver used in England for coinage would be 925, and that used in France and Germany for the same purpose would be 900. The fineness of the silver alloys which are to be employed for different purposes is regulated by law in some countries.

The quantity of silver contained in an alloy with copper was formerly exclusively determined by *cupellation*. In this process the sample of silver is mixed with lead and heated on a small flat crucible made of bone-ash (the cupel) in a current of air; the lead and the copper are then oxidized, and their oxides are absorbed by the porous bone-ash of the cupel. Finally, there remains behind a button of pure silver, from the weight of which the fineness of the sample may be easily calculated. A quicker and more accurate process is the wet way introduced by Gay-Lussac. In this method the silver is dissolved in nitric acid and a normal solution of common salt added until the whole of the silver is precipitated as silver chloride. For the details of this method the student must consult a text-book of analytical chemistry.

Detection of Silver Compounds.

The reduction of any compound of silver when mixed with sodium carbonate and heated on charcoal before the blowpipe, and the production of a white globule of metallic silver which does not oxidize in the air, the precipitation of black silver sulphide when

sulphuretted hydrogen is led through an acid solution of a silver salt, and, above all, the formation of silver chloride by hydrochloric acid, make it very easy to detect the presence of silver and to separate it from other metals. Silver chloride may be distinguished from lead chloride by the solubility of the latter salt in hot water, and from mercurous chloride by the action of ammonia. This dissolves the silver chloride, but converts the mercurous salt into a black compound (p. 543).

GOLD.

Chemical Symbol: Au.—*Atomic Weight*: 196·6.

Gold is chiefly found in nature in the free state, sometimes pure and well crystallized, but usually containing silver. It occurs in quartz rocks or in alluvial quartz sand which has been deposited by the disintegration of the older rocks. These auriferous sands, which often cover a considerable extent of country, are washed by suitable arrangements, on a small or large scale, when the lighter particles of sand and mud are carried away and the heavier particles of gold remain behind. The gold is then brought into the market in this form, or if in a finely divided state is extracted with mercury, which is afterwards removed by distillation. Gold is now chiefly obtained from California and Australia, but is found in smaller quantities in other parts—*e.g.* in the Ural Mountains, in Hungary and Transylvania, and in Africa. Small quantities of gold have also been found in Cornwall and Wales. Chemical compounds of gold rarely occur in nature—*sylvanite* or *graphic tellurium*, found in Transylvania, is a compound of gold and tellurium. Many silver ores and some argentiferous lead ores, as well as some specimens of copper-pyrites, contain small quantities of gold. In the silver ores the gold is extracted with the silver, and the two metals are afterwards separated by nitric acid.

Gold is one of the few metals which have a decided tint, and is distinguished from all others by its yellow colour. It crystallizes in the regular system, is very soft, considerably more so than silver, and very malleable. In extremely thin leaves (gold-leaf), it transmits bluish-green light. Gold melts more difficultly than silver, but somewhat more easily than copper, and volatilizes at very high temperatures. Its specific gravity is 19·3.

Gold does not directly unite with oxygen at any temperature, but easily combines with chlorine. Hydrochloric, sulphuric, or nitric acid has no action on the metal, but aqua regia dissolves gold and produces a yellow solution of auric chloride. From this solution the metal may be again precipitated by various reducing agents, such as ferrous sulphate, oxalic acid, sulphurous acid, or metallic iron. The best substance to employ for the precipitation of gold from a solution of its chloride is a cold saturated solution of ferrous sulphate, which is then oxidized to a mixture of ferric sulphate and ferric chloride. The gold is thrown down as a brown powder, which acquires the colour and lustre of the metal when rubbed. This method is used to separate pure gold from a solution containing copper and other metals.

Compounds of Gold.

Gold forms two series of compounds in which the element exists, as a triad and as a monad respectively, and which are distinguished as the *auric* and *aurous* compounds. The metal only possesses weak affinities for other elements, and its two oxides are such weak bases that their salts are hardly known. The most important auric compound is

Auric Chloride : $AuCl_3$, which is obtained by dissolving pure gold in aqua regia and remains as a reddish brown deliquescent mass when the solution is evaporated to dryness. It not only dissolves in water, but also in alcohol and ether, and to such an extent in the latter liquid that the chloride is abstracted from its aqueous solution when this is shaken with ether. A solution of auric chloride produces a purple stain of reduced gold when a drop is allowed to fall on the skin, and gives a purple precipitate when mixed with stannous chloride—see Purple of Cassius (p. 556). When heated, the salt decomposes into chlorine and aurous chloride.

Auric chloride forms soluble crystalline double salts with hydrochloric acid and soluble chlorides. The hydrochloric acid compound: $AuCl_3,HCl + 3H_2O$, or $HAuCl_4 + 3H_2O$, is deposited from a hot acid solution of auric chloride in long yellow needles. On mixing a solution of auric chloride with one of the chlorides of potassium, sodium, or ammonium, and evaporating down, crystals of the compounds : $2(AuCl_3,KCl) + H_2O$, or $2KAuCl_4 + H_2O$; $AuCl_3,NaCl + 2H_2O$, or $NaAuCl_4 + 2H_2O$, and $2AuCl_3,NH_4Cl + 5H_2O$, or $2NH_4AuCl_4 + 5H_2O$ are obtained. The sodium compound is much

less deliquescent than pure auric chloride, and is the form in which this salt is usually brought into trade. It is sold as *non-deliquescent chloride of gold* in 15 grain or 1 gramme tubes.

Auric Oxide: Au_2O_3, is obtained by digesting a solution of auric chloride with an excess of magnesia. The brown powder so produced consists of a compound of auric oxide and magnesia (magnesium aurate) with the excess of magnesia. When this powder is treated with strong nitric acid, the magnesia is all dissolved and auric oxide remains behind as a brown powder. It is decomposed by light or heat into gold and oxygen. If the brown compound of auric oxide and magnesia is digested with dilute instead of concentrated nitric acid, *auric hydrate*: $Au(OH)_3$, remains behind as a reddish yellow powder.

Auric oxide is so weak a base that neither it nor the hydrate can unite with oxyacids to form salts. On the other hand, it can combine with bases and form salts in which it plays the part of an acid. Hence auric oxide may be considered as the anhydride of an acid—*auric acid.*

Potassium Aurate: $AuO \cdot OK + 3H_2O$.—Auric oxide or hydrate easily dissolves in caustic potash, and when the solution is evaporated, finally in a vacuum, potassium aurate separates in bright yellow needles. Its solution reacts alkaline and gives precipitates of insoluble aurates when mixed with the salts of other metals.

If a solution of auric chloride is digested with an excess of ammonia a yellowish brown powder is produced, which violently explodes when slightly warmed or rubbed. The composition of this *fulminating gold* is unknown.

Auric Cyanide: (?) $AuCy_3 + 3H_2O$.—Nearly all the cyanides of the heavy metals are insoluble in water, but mercuric cyanide and auric cyanide are exceptions to this rule. If a solution of auric chloride is mixed with a hot concentrated solution of potassium cyanide, the compound *potassium-auric cyanide*: $KCy,AuCy_3 + H_2O$, or $KAuCy_4 + H_2O$, crystallizes out on cooling in colourless plates. This substance, when dissolved in water, gives a white curdy precipitate with a solution of silver nitrate of the corresponding silver salt. If this silver-auric cyanide is carefully washed, mixed with water, and then a quantity of hydrochloric acid added insufficient to produce complete decomposition, silver chloride, hydrocyanic acid, and auric cyanide are produced, and

when the clear liquid is evaporated in a vacuum over sulphuric acid this salt remains behind as a white crystalline mass. By recrystallizing from its alcoholic solution, the auric cyanide may be obtained as large crystalline tablets or plates. The salt is easily decomposed when heated. (See Appendix.)

Auric Sulphide: Au_2S_3 (?).—It is still doubtful whether the black precipitate which is produced when sulphuretted hydrogen is led through a cold solution of auric chloride consists of auric sulphide, or is a compound of aurous and auric sulphides. The precipitate easily dissolves in solutions of alkaline sulphides. If gold is fused with potassium polysulphide (liver of sulphur), a double sulphide of potassium and gold is formed, which dissolves when the cold mass is digested with water. From this solution acids precipitate a sulphide of gold.

The following more important aurous *compounds* may be described.

Aurous Chloride: AuCl.—Auric chloride when heated decomposes into chlorine and aurous chloride or gold, according to the temperature employed. If the temperature does not exceed 200°, aurous chloride remains behind as a dirty-white powder which is insoluble in water. It is decomposed into auric chloride and metallic gold when boiled with water.

Aurous Oxide: Au_2O.—Aurous chloride when digested with caustic potash is converted into a dark-violet coloured powder of aurous oxide. The compound is insoluble in water, and is not changed by sulphuric or nitric acid. Hydrochloric acid decomposes it into auric chloride and gold. Oxy-salts of aurous oxide are not known if we except the crystalline salt which separates from a mixed solution of auric chloride and sodium thiosulphate on the addition of alcohol, and which may be a double salt of aurous and sodium thiosulphates.[1]

Aurous Cyanide: AuCy.—Fulminating gold readily dissolves in a warm solution of potassium cyanide, and the solution deposits large prisms of *potassium-aurous cyanide*: KCy,AuCy or $KAuCy_2$, on cooling. Hydrochloric acid separates aurous cyanide from this salt, and the cyanide may be obtained by evaporating to dryness and extracting with water, when it remains as a yellow crystalline powder insoluble in water. Potassium cyanide easily redissolves it; it is decomposed when heated into gold and cyanogen.

[1] A similar double sulphite is also known.

Purple of Cassius is a compound of gold, tin, and oxygen, of varying and, therefore, uncertain composition. It is thrown down as a beautiful purple precipitate by adding a mixture of stannous and stannic chlorides to a dilute solution of auric chloride. If concentrated solutions of these salts are mixed, the precipitate possesses a brown colour. The compound may also be prepared by acting on an alloy of gold, silver, and tin with nitric acid. The silver then dissolves and purple of Cassius remains behind. Purple of Cassius is used in painting on porcelain and glass to produce a beautiful red tint.

Alloys of Gold.

Pure gold is used for the manufacture of gold-leaf, and in the finely divided state, as obtained by precipitation with ferrous sulphate, for gilding porcelain. The gold is mixed with a suitable material and painted on the porcelain, and when the articles are afterwards heated in a kiln the metal burns into the glaze. Articles made of the base metals may be covered with a thin layer of gold (or gilt) in various ways. According to one method a gold amalgam is rubbed on the surface to be gilt, the mercury afterwards expelled by heating, and the rough surface polished by burnishing. In the wet way, a thin coating of gold is obtained by simple immersion in an alkaline solution of auric chloride, or better by a separate electric current. In the process of *electro-gilding* the object to be gilt is dipped in a warm solution of one of the double cyanides of gold and potassium and made the negative pole of an electric current. The coating of gold obtained in this way is far more durable and compact than that produced by any other process.

The gold which is used by the goldsmith and for coinage is an alloy of the metal with copper and sometimes silver. This alloy not only melts more easily, but is also harder and does not so readily wear away when used. In England the fineness of a sample of gold is expressed in *carats*; pure gold being said to be 24 carats. Thus 18 carat gold consists of 18 parts of gold alloyed with 6 parts of copper. English sovereigns and half-sovereigns are made of 22 carat gold, or contain 916·66 parts of pure gold per thousand (or *mille*). The gold used for coinage in Germany and some other countries has a fineness of 900, or contains 900 parts of pure gold per thousand, which corresponds to 21·6 carat gold; 15 or 12 carat gold is usually employed for the manufacture of jewellery.

PLATINUM METALS.

THIS group of the noble metals includes, besides platinum, the five metals: iridium, palladium, rhodium, ruthenium, and osmium. They are almost always associated with one another in nature and are found native accompanying platinum. The so-called platinum ore contains them as alloys together with varying quantities of gold, copper, and iron. This ore is found in the Ural, in South America, California, Borneo, Australia, and a few other localities, and, like gold, usually in alluvial sands.

These six metals closely resemble one another in many points, but in some respects differ strikingly. Such a difference is noticed, for example, when we compare together their specific gravities and their atomic weights. It is then seen that the three: platinum, iridium, and osmium, possess a specific gravity and atomic weight which are about double those of the other three: palladium, rhodium, and ruthenium. These differences are exhibited in the following table:—

	Specific gravity	Atomic weight		Specific gravity	Atomic weight
Platinum	21·5	194·3	Palladium	11·4	106·4
Iridium	22·4	192·5	Rhodium	12·1	102·7
Osmium	22·5	190·3	Ruthenium	12·3	101·4

A second difference between these metals is their behaviour with regard to oxygen. Most of them have so weak an affinity for oxygen that they not only do not unite directly with this element, but the majority of their oxides, when prepared in an indirect manner, lose their oxygen when heated. On the other hand, osmium and ruthenium combine energetically with oxygen when simply heated in the air and produce volatile compounds of an acid character.

Of the six rare platinum metals, platinum itself is found in far larger quantities than the other five. On this account, and because the metal is used for many purposes in the arts, the compounds of platinum are better known than those of the other metals. But the majority of these compounds are only of chemical interest.

PLATINUM.

Chemical Symbol: Pt.—*Atomic Weight*: 194·3.

In the extraction of platinum the ore is first warmed with dilute aqua regia, to dissolve any gold, and then treated with stronger aqua regia, often under pressure, when platinum with traces of iridium and rhodium go into solution as chlorides. The residue consists chiefly of the earthy impurities and of an alloy of osmium and iridium (*osmiridium*) which is not attacked by aqua regia. The solution is evaporated to dryness, then digested with water, and the clear liquid mixed with a solution of ammonium chloride. A yellow crystalline double chloride of platinum and ammonium is thus produced which is difficultly soluble in water and insoluble in alcohol. The salt is filtered off, washed, dried, and then heated to redness, when metallic platinum remains behind as a grey spongy mass, called *spongy-platinum*. This is the material used for the preparation of vessels made of platinum; it still contains traces of iridium (and rhodium). Very various and often complicated processes are used to completely separate platinum from all the other platinum metals and to prepare it perfectly pure, for a description of which the student must consult a larger book. Small quantities of pure platinum may be prepared by the following method, due to Bunsen. The solution of the chlorides is mixed with a large excess of caustic soda until the precipitate which is first produced is redissolved and then boiled with the addition of a few drops of alcohol. During this boiling, the platinum tetrachloride remains unchanged, but the tetrachlorides of the other metals are reduced to a dichloride or a sesqui-chloride, and these do not yield an insoluble compound with ammonium chloride. When, therefore, the alkaline solution is afterwards acidulated with hydrochloric acid and mixed with an excess of ammonium chloride, the platinum alone is precipitated, and the other metals remain in solution.

Platinum is a greyish-white metal of specific gravity 21·5; it is malleable and ductile, and very tough, and indeed, scarcely less so than iron. Small quantities of iridium render it less malleable, but at the same time make it harder and tougher and more suitable for the manufacture of crucibles, dishes, &c. It cannot be fused at the temperature of our furnaces, but readily melts in the oxy-hydrogen flame, when heated in a lime crucible (p. 24). Thin

platinum wire melts easily in the oxy-hydrogen blowpipe, and is even partly volatilized.

Platinum shares with iron the property of welding at a high temperature. Two pieces of platinum heated to whiteness, but still far below the melting point of the metal, may be welded together under the hammer. In the same way, the spongy platinum which remains behind when ammonium-platinum chloride is heated, may be welded into a compact mass under strong pressure at a high temperature. Such platinum, however, still contains traces of air, and crucibles made of it often become covered with small excrescences due to the expansion of this confined air.

Platinum may be obtained in a still more finely divided state than it exists in spongy platinum. We are acquainted with the metal in the form of a loose very fine black powder, called *platinum black*. This form of platinum may be obtained by the reduction of an alkaline solution of platinic, or better, platinous chloride. For this purpose platinous chloride is dissolved in an excess of caustic potash (or soda), the mixture heated to boiling, and small quantities of alcohol gradually added. The metal is then reduced and the alcohol oxidized to aldehyde and acetic acid. This black powder, when carefully washed and dried at a low temperature, absorbs and condenses considerable quantities of various gases, especially oxygen, and is therefore a powerful oxidizing agent.

Spongy platinum also possesses this property of condensing gases, but in a less degree. If a jet of hydrogen is allowed to play on a small piece of spongy platinum in the air, the platinum first becomes red hot and then ignites the hydrogen. Döbereiner's hydrogen lamp depends upon this property of spongy platinum. The oxygen which is condensed in the spongy platinum has stronger affinities than the ordinary gas, and as platinum also condenses hydrogen, the two substances are brought close enough together to cause their union.

Compact metallic platinum offers a far less surface to the gases than the spongy metal; it acts therefore less energetically, and not at all at the ordinary temperature. But if a spiral of platinum wire or a piece of thin platinum foil is heated to low redness and suspended in a vessel containing a little ether, the vapour of the ether, which is contained in the vessel mixed with air, gradually becomes oxidized to aldehyde and acetic acid, with so much evolution of heat that the platinum spiral remains glowing, and

that the ether sometimes catches fire. It has already been mentioned (p. 162) that compact platinum, when heated, can convert a mixture of sulphurous anhydride and oxygen into sulphuric anhydride without itself undergoing any change. Platinum black, containing the metal in its most finely divided state, acts more powerfully than either the spongy or compact metal. It can absorb as much as 200 times its volume of oxygen, or even more, and we may therefore suppose that the gas is condensed by it to the liquid or even solid state. If platinum black is moistened with alcohol and exposed to the air, the latter substance becomes oxidized to aldehyde and acetic acid, and so much heat is set free that the metal is raised to redness and continues to glow for some time.

Platinum is not attacked by either nitric, hydrochloric, or sulphuric acid, but dissolves in aqua regia with formation of platinic chloride. Molten caustic alkalies, especially lithia, attack platinum at a red heat, and a mixture of fused caustic potash and nitre acts more powerfully. Sodium or potassium carbonate is entirely without action on the metal even at a white heat. Sulphur, phosphorus, and arsenic also slowly attack compact platinum, and the spongy metal readily melts when heated with these substances. A mixture of silicates and charcoal also attacks platinum, with formation of a compound of platinum and silicon, and platinum crucibles are therefore soon destroyed if brought into direct contact with glowing charcoal.

Many of the easily fusible heavy metals, such as lead, form easily fusible alloys with platinum. If, for example, a piece of lead is melted in a platinum crucible, an easily fusible alloy of platinum and lead is formed, and a hole is produced in the bottom of the crucible. Care must, therefore, be taken that these substances (sulphur, phosphorus, arsenic, and the easily fusible heavy metals), or mixtures which might produce them, are never strongly heated in platinum vessels.

The properties which are possessed by platinum—its infusibility at any temperature of our furnaces, that it does not unite with oxygen at any temperature, and that it resists the action of all acids including hydrofluoric acid, but excepting aqua regia—make the metal simply indispensable to the chemist. We employ it in the form of wire, foil, crucibles and dishes, tongs, tubes, retorts, &c. Considerable quantities of platinum are now used in the arts for the manufacture of large retorts and coolers in the purification of sulphuric acid. Platinum coins were also formerly used in Russia,

but have now been withdrawn from circulation. Notwithstanding its scarcity, platinum is more than one-third cheaper than gold, but is about seven times as dear as silver.

Compounds of Platinum.

Platinum unites with other elements and produces two series of compounds—the *platinous* and *platinic* compounds—in which the metal is a diad and a tetrad respectively. The compounds of platinum thus resemble those of carbon and tin. The most interesting of these substances are the chlorides and the peculiar platinum bases.

Platinic Chloride: $PtCl_4$.—On dissolving platinum in aqua regia and evaporating the solution to dryness with an excess of hydrochloric acid, a brownish-red crystalline and deliquescent mass remains behind of the composition: $2HCl,PtCl_4$ or $H_2PtCl_6 + 6H_2O$. If, however, excess of the acid is avoided, platinic chloride: $PtCl_4 + 5H_2O$, is obtained in fine red crystals. Both dissolve in water and produce a reddish-yellow liquid with an acid reaction.[1] Alcohol and ether also dissolve platinic chloride in the cold, but are oxidized with reduction of the chloride when the solution is warmed. When carefully heated, platinic chloride loses one-half of its chlorine and becomes converted into platinous chloride; if more strongly heated, it is completely converted into platinum and chlorine.

Platinic chloride readily combines with the chlorides of the alkali-metals, of thallium and of the metals of the alkaline earths, producing double chlorides in which the chlorine combined with the platinum is twice as much as that united with the other metals. These salts are mostly difficultly soluble in water and insoluble in alcohol, and separate or crystallize out when solutions of the two chlorides are mixed. They usually crystallize in regular octahedra.

These double chlorides have all a similar composition to the hydrochloric acid compound referred to above: $2HCl,PtCl_4$ or H_2PtCl_6, and may be considered as salts of this *chlorplatinic acid*. *Potassium chlorplatinate*: $2KCl,PtCl_4$ or K_2PtCl_6, is a pale yellow crystalline precipitate produced when solutions of potassium and

[1] The brownish colour which a solution of platinic chloride sometimes possesses is due to the presence of traces of iridium and other impurities.—ED.

platinic chlorides are mixed, and which is only completely precipitated on the addition of alcohol. When heated it breaks up into platinum, chlorine and potassium chloride, the last of which may be extracted by boiling the residue with water. *Ammonium chlorplatinate*: $2NH_4Cl,PtCl_4$ or $(NH_4)_2PtCl_6$, closely resembles the potassium salt. When gently heated it leaves a residue of pure platinum as a grey spongy mass. *Sodium chlorplatinate*: $2NaCl,PtCl_4$ or $Na_2PtCl_6 + 6H_2O$, differs from the above double salts in that it crystallizes with water, and dissolves both in water and alcohol. The latter property enables us to completely separate sodium compounds from those of potassium. The sodium and potassium salts are first converted into chlorides, an excess of platinic chloride then added to this solution and evaporated to dryness. The residue is then extracted with strong alcohol when the sodium chlorplatinate and the excess of platinic chloride dissolve, leaving the insoluble potassium salt behind. If an excess of platinic chloride had not been added, some sodium chloride, which is insoluble in alcohol, would remain with the potassium chlorplatinate. Sodium chlorplatinate crystallizes from its concentrated aqueous solution in reddish-yellow prisms.

Platinous Chloride: $PtCl_2$.—If platinic chloride is carefully heated to 230° in a porcelain basin with continued stirring until no further odour of chlorine is perceived, it is completely converted into platinous chloride and chlorine. This latter compound is an olive-green powder, insoluble in water, but dissolving in hydrochloric acid to form a dark-brown solution. It is converted by aqua regia into platinic chloride. Platinous, like platinic chloride, unites with other chlorides (of potassium, ammonium, &c.) and produces crystalline double salts, which are soluble in water. The compounds which it forms with ammonia are described below.

Platinic Oxide: PtO_2, and **Platinic Hydrate**: $PtO_2.nH_2O$.—If a solution of platinic chloride is mixed with one of sodium carbonate, the precipitate which is produced is not platinic carbonate, but is a compound of soda and platinic oxide. If the whole is then evaporated to dryness and extracted with dilute acetic acid, platinic hydrate remains behind as a compact reddish-brown powder. The compound does not dissolve in this acid, but produces, with the stronger oxy-acids, soluble platinic salts, which

have as yet been but little investigated. The hydrate also unites with strong bases and produces compounds (*platinates*), in which it plays the part of an acid. When gently heated the hydrate is converted into a black powder of *platinic oxide*, which is insoluble in acids.

Platinous Oxide : PtO, and **Platinous Hydrate** : $Pt(OH)_2$. Platinous chloride when digested with caustic potash is converted into a dark-brown powder of platinous hydrate, which is insoluble in water, but dissolves both in strong caustic potash and in acids, producing brown solutions in both cases. When the hydrate is gently heated, *platinous oxide* remains as a black powder insoluble in acids.

Platinic Sulphide: PtS_2, and *Platinous Sulphide*: PtS, are black precipitates produced when sulphuretted hydrogen is led through a solution of platinic or platinous chloride respectively. They both behave as sulpho-acids and dissolve, for example, in potassium sulphide to form red solutions.

Platinous Cyanide : $PtCy_2$.—If platinum black is boiled with a concentrated solution of potassium cyanide, crystals of *potassium-platinous cyanide* : $2KCy, PtCy_2 + 3H_2O$ or $K_2PtCy_4 + 3H_2O$, separate on evaporation. The crystals show a beautiful dichroism—*i.e.* they appear of different colours when viewed in different directions. From a solution of this salt, dilute acids separate platinous cyanide as a greenish-yellow powder insoluble in water and acids. It unites with other cyanides and forms other double salts, similar in composition to the potassium compound, and of which some are soluble, and some insoluble, in water.

Ammoniacal Compounds of Platinum.

Under this name is included a number of very interesting compounds, produced by the action of ammonia on platinous chloride and by further changes in the primary compound. In these compounds a portion of the hydrogen of ammonium is displaced by diad platinum : Pt'', or by the diad radicals : (PtCl)'', (PtO)'', or even by ammonium itself.

Substitution of the hydrogen in ammonia or in an ammonium compound by a *diad* radical may take place in two different ways.

Either two atoms of hydrogen may be displaced in *one* molecule of ammonia by the diad radical, or one atom of hydrogen may be symmetrically displaced from each of *two* molecules of ammonia by the radical.

The compounds of the first kind are unstable, and readily pass into ordinary compounds of ammonia.

The second class of compounds—the *diammonium* compounds—are more stable and do not easily pass into compounds of *ordinary ammonia.*

The ammoniacal compounds of copper, some of those of mercury, and possibly those of cobalt, belong to this class of diammonium compounds, but far more important representatives of the same group are those which contain platinum. The simplest of these is: *platinoso-diammonium chloride*: $Pt''\begin{cases}NH_3Cl\\NH_3Cl\end{cases}$—*i.e.* a compound consisting of two molecules of ammonium chloride in which two atoms of hydrogen (one from each molecule) are displaced by one atom of diad platinum. The following compounds may serve as types of this very numerous group:—

(i.) Platinoso-diammonium chloride . .	$Pt''\begin{cases}NH_3Cl\\NH_3Cl\end{cases}$
(ii.) Diammon-platinoso-diammonium chloride . .	$Pt''\begin{cases}NH_2(NH_4)Cl\\NH_2(NH_4)Cl\end{cases}$
(iii.) Diammon-platinoso-diammonium hydrate . .	$Pt''\begin{cases}NH_2(NH_4)OH\\NH_2(NH_4)OH\end{cases}$
(iv.) Chlorplatin-diammonium chloride .	$PtCl_2''\begin{cases}NH_3Cl\\NH_3Cl\end{cases}$
(v.) Diammon-chlorplatin-diammonium chloride .	$PtCl_2''\begin{cases}NH_2(NH_4)Cl\\NH_2(NH_4)Cl\end{cases}$
(vi.) Oxyplatin-diammonium nitrate . .	$PtO''\begin{cases}NH_3\cdot ONO_2\\NH_3\cdot ONO_2\end{cases}$
(vii.) Diammon-oxyplatin-diammonium nitrate . .	$PtO''\begin{cases}NH_2(NH_4)\cdot ONO_2\\NH_2(NH_4)\cdot ONO_2\end{cases}$

These salts are partly crystalline and soluble in water. The following is a brief account of the methods used for obtaining them.

If ammonia is gradually added to a solution of platinous chloride in dilute hydrochloric acid, a green crystalline salt separates out, which is a double compound of diammon-platinoso-diammonium chloride with platinous chloride:—

$$Pt''\begin{cases}NH_2(NH_4)Cl\\NH_2(NH_4)Cl\end{cases} + PtCl_2.$$

This is commonly known as the *green salt of Magnus*, because it was discovered by this chemist; it may also be prepared from its separate constituents. If this double salt, or if platinous chloride (dissolved in hydrochloric acid) is heated with an excess of ammonia, the compound diammon-platinoso-diammonium chloride: (ii.): $Pt''\begin{cases}NH_2(NH_4)Cl\\NH_2(NH_4)Cl\end{cases}$ crystallizes out in fine needles. The following equation illustrates its production:—

$$PtCl_2 + 4NH_3 = Pt''\begin{cases}NH_2(NH_4)Cl\\NH_2(NH_4)Cl\end{cases}$$

If the two atoms of chlorine which this salt contains are displaced by hydroxyl, the corresponding base (iii.): $Pt''\begin{cases}NH_2(NH_4)OH\\NH_2(NH_4)OH\end{cases}$ is produced; this crystallizes from its solutions and caustic potash expels no ammonia from it. It is a powerful base, and forms numerous salts with acids. When this base is heated, it parts with 2 molecules of ammonia and is converted into *platinoso-diammonium hydrate*: $Pt''\begin{cases}NH_3OH\\NH_3OH\end{cases}$ a substance which is no longer soluble in water, and which gives insoluble explosive compounds with acids. Similarly, if the chloride (ii.) is heated to a temperature not exceeding 270°, it also loses 2 molecules of ammonia, and becomes platinoso-diammonium chloride (i.): $Pt''\begin{cases}NH_3Cl\\NH_3Cl\end{cases}$ a salt which is only slightly soluble in water, and which readily again takes up 2 molecules of ammonia when boiled with this substance.

If chlorine is led into water which contains platinoso-diammonium chloride in suspension, each molecule of the salt combines with 2 atoms of chlorine and the diad platinum is changed into the diad radical $(PtCl_2)''$, containing the metal in the tetrad form. The salt then produced is chlorplatin-diammonium chloride (iv.), according to the equation:—

$$Pt''\begin{cases}NH_3Cl\\NH_3Cl\end{cases} + Cl_2 = (Pt^{iv}Cl_2)''\begin{cases}NH_3Cl\\NH_3Cl\end{cases}$$

This salt, which thus contains its 4 atoms of chlorine differently united, is only slightly soluble in water, and when boiled with ammonia takes up 2 molecules and becomes diammon-chlorplatin

diammonium chloride (v.): $(PtCl)_2'' \begin{cases} NH_2(NH_4)Cl \\ NH_2(NH_4)Cl \end{cases}$ a salt which may be also produced by leading chlorine into a solution of diammon-platinoso-diammonium chloride (ii.).

Oxyplatin-diammonium nitrate (vi.): $(Pt^{iv}O)'' \begin{cases} NH_3 \cdot ONO_2 \\ NH_3 \cdot ONO_2 \end{cases}$ may be obtained from chlorplatin-diammonium chloride (iv.) by long boiling with an excess of silver nitrate, and when heated with ammonia yields diammon-oxyplatin-diammonium nitrate (vii.): $(PtO)'' \begin{cases} NH_2(NH_4)ONO_2 \\ NH_2(NH_4)ONO_2 \end{cases}$ which crystallizes well from hot water.

Similarly constituted diammonium compounds containing a diad radical are known in organic chemistry. (See Appendix.)

PALLADIUM.

Chemical Symbol: Pd.—*Atomic Weight*: 106·4.

Platinum ores only contain a very small quantity of palladium—at most one or two per cent., and the metal is usually prepared from a gold ore which contains it, and which occurs in Brazil. This ore is fused with silver, then granulated and digested with nitric acid, which extracts the silver and palladium and leaves the gold behind. The solution is mixed with sodium chloride to precipitate the silver, and the palladium is then thrown down from the filtrate as palladous cyanide by the addition of mercuric cyanide. When heated to redness the cyanide yields the metal, which may then be fused in the oxy-hydrogen flame. Palladium melts more easily than platinum, and is, in fact, the most easily fusible of all the platinum metals, but it can only be melted with considerable difficulty in a wind furnace. Palladium resembles platinum in its external appearance, but is only about half as heavy: its specific gravity is 11·4. It is further distinguished from platinum by its solubility in nitric acid, and it is even attacked by warm concentrated sulphuric acid. It is malleable and ductile, and may be welded at a white heat. When heated in the air the metal tarnishes, but regains its original lustre when the temperature is raised to a bright red heat.

Palladium Hydride: Pd_2H.—The most remarkable property of palladium, a property which is not possessed by any other metal

to a similar extent, is its power of absorbing and retaining large quantities of hydrogen. The metallic appearance of the compound of palladium and hydrogen reminds one of an alloy, and appears to prove that hydrogen is a gaseous metal. Its composition is Pd_2H, which corresponds to 600 volumes of hydrogen to one volume of the metal. (See App.) The compound is formed at the ordinary temperature when palladium is brought into an atmosphere of hydrogen, but the most favourable temperature for its formation is 100°. Above 130° and under the ordinary atmospheric pressure it begins to decompose with evolution of hydrogen, but the gas can only be completely expelled by protracted glowing. Besides the hydrogen which is chemically united with the metal, it can also absorb the gas mechanically. If water is electrolysed and palladium, especially if in the spongy form, used for the negative pole, the metal can absorb nearly 1,000 times its volume of the gas. But it readily loses the excess of hydrogen which it then contains beyond that combined chemically, and at 100° the whole of the hydrogen mechanically absorbed is expelled. If a piece of palladium which has thus been saturated with hydrogen is exposed to the air, the gas is rapidly oxidized to water, with a considerable evolution of heat; and if placed in a solution of potassium ferricyanide the salt is rapidly reduced to potassium ferrocyanide. Such palladium hydride when saturated with hydrogen is, in fact, one of the most powerful of reducing agents. It may be preserved for a long time unchanged if quickly placed in cold boiled water or alcohol.

This property which palladium possesses of combining both chemically and mechanically with hydrogen, explains why hydrogen when led through a palladium tube heated to 130° diffuses through the walls as if they were porous. At a red-heat hydrogen diffuses still more readily through the metal.

Palladium plays the part of a diad and tetrad in its compounds. We are acquainted with a palladous oxide: PdO, and a corresponding palladous chloride: $PdCl_2$, with a palladic oxide: PdO_2, and with palladic chloride: $PdCl_4$. (See Appendix.)

On dissolving the metal in nitric acid, a brown solution is produced which contains *Palladous nitrate*: $(NO_2)_2O_2Pd$, and which yields yellowish brown deliquescent prisms when evaporated to a syrup. The solution serves to detect iodine and to separate this substance from bromine and chlorine, since palladous iodide is quite insoluble in water, while the corresponding bromide and

chloride dissolve easily. If the dry salt is carefully heated as long as nitrous fumes are evolved, *palladous oxide*: PdO, remains behind as a black powder scarcely soluble in acids.

If palladium is dissolved in aqua regia, a dark-brown liquid results, which contains *palladic chloride*: $PdCl_4$; and if this solution is mixed with the alkaline chlorides, similar double salts to those containing platinic chloride are produced.

Potassium Chlorpalladinate: $2KCl,PdCl_4$ or K_2PdCl_6, crystallizes in dark red octahedra. When small quantities of caustic potash are added to this salt a dark yellow powder of palladic hydrate containing potash is produced. And this when washed with warm water leaves a residue of black *palladic oxide*: PdO_2, which is scarcely attacked by oxy-acids.

When the solution of palladium in aqua regia is evaporated down, it loses chlorine and is converted into *palladous chloride*, which crystallizes out when the solution is slowly evaporated as brownish-red prisms of the composition: $PdCl_2 + 2H_2O$, and which do not deliquesce in the air. This chloride also produces crystalline double salts with the alkaline chlorides. A solution of palladous chloride in water is a very delicate reagent for carbonic oxide. The smallest quantities of this gas when brought into contact with the solution cause reduction and separation of black palladium.

Palladous Iodide: PdI_2, is quite insoluble in water and in dilute acids; it is obtained as a black precipitate when a soluble iodide is added to a solution of palladous nitrate. The corresponding chloride and bromide are soluble in water.

Palladous chloride unites with ammonia and produces compounds similar to the ammoniacal compounds of platinum (p. 563).

IRIDIUM.

Chemical Symbol: Ir.—*Atomic Weight*: 192·5.

Iridium resembles platinum in many respects, and only differs from this metal in some of its less important properties. Its specific gravity is 22·4; and it is harder and more brittle, and much more

difficultly fusible than platinum. In the compact state iridium is not acted upon by aqua regia; it is only dissolved when in a finely divided state as iridium-black. The metal may be oxidized by heating it strongly with a mixture of caustic potash and nitre.

Iridium is contained in the so-called platinum residues which remain after the ore has been digested with aqua regia. It is usually present united with osmium as an alloy of *osmiridium* in the form of very hard granules. This alloy may be decomposed by mixing it with common salt and heating the mixture in a stream of moist chlorine. The osmic chloride which is then produced is decomposed by the water contained in the moist gas, and converted into osmic acid, which is a volatile compound and which condenses in a receiver attached to the other end of the tube in which the mixture is heated; at the same time the iridium becomes sodium-iridium chloride. The residue remaining in the tube and containing this salt is extracted with water, mixed with excess of sodium carbonate and evaporated to dryness. The dry mass when heated to redness yields iridium sesquioxide, which remains when the sodium chloride and carbonate are dissolved in water, and which is easily reduced to metallic iridium when gently heated in a stream of hydrogen.

Besides the compounds of iridium with oxygen and chlorine which correspond to those of platinum with the same elements—*i.e. iridic oxide*: IrO_2, *iridious oxide*: IrO, *iridic chloride*: $IrCl_4$, and *iridous chloride*: (?) $IrCl_2$, it also forms *iridium sesquioxide*: Ir_2O_3, and *iridium sesquichloride*: (?) Ir_2Cl_6, and *iridium trioxide*: IrO_3. The sesquioxide is obtained as a black powder by heating sodium-iridium chloride with sodium carbonate, and washing with water (see above). Iridium sesquichloride is obtained when iridium is strongly heated in chlorine as a yellowish-brown amorphous mass, insoluble in water and acids.

Iridic Chloride: $IrCl_4$, is obtained by dissolving the sesquioxide in aqua regia. It is much darker in colour than platinic chloride, and its solution is of a dark-brown colour. It produces double salts with the alkaline chlorides similar to those of platinum, but much darker in colour. *Potassium-iridium chloride*: $2KCl,IrCl_4$ or K_2IrCl_6, forms small blackish-red octahedra, almost insoluble in cold water and only dissolving slightly when warmed. The ammonium salt is very similar.

RHODIUM.

Chemical Symbol: Rh.—*Atomic Weight*: 102·7.

This rare element only occurs in very small quantities in platinum ores, and has therefore been but little studied. In its chemical properties it is most closely related to iridium. Rhodium is a malleable and ductile metal, more easily fusible than iridium, but less so than platinum, and is insoluble in aqua regia, except when alloyed with platinum, in which case it dissolves with this metal. When heated in the air it oxidizes slightly. Its oxides correspond to those of iridium. The only chloride known is the *sesquichloride* : (?)Rh_2Cl_6.

OSMIUM.

Chemical Symbol: Os.—*Atomic Weight*: 190·3.

The separation of this metal from iridium has been described on the preceding page. If the vapours of osmic acid are led into caustic potash, the resulting liquid evaporated to dryness with much ammonium chloride, and the dry residue heated to redness, metallic osmium remains behind as a black powder when the fused mass is extracted with water. The metal remains unmelted at the highest temperatures; even in the oxy-hydrogen flame it only becomes a little more dense. It may be obtained as a hard crystalline powder when fused with tin, and the tin afterwards removed by hydrochloric acid. *Osmium has a specific gravity of 22·5, and is apparently the densest of all substances.* Aqua regia, or even nitric acid, oxidizes osmium to osmic acid. In the finely divided state, the metal burns when heated in the air, and produces the same substance.

The compounds of osmium with oxygen and chlorine mostly correspond to those of platinum, thus: *osmous oxide*: OsO, and *osmic oxide*: OsO_2, *osmous chloride*: $OsCl_2$, and *osmic chloride*: $OsCl_4$, and besides these an *osmous anhydride* : OsO_3. (See App.) The most important and interesting of the osmium compounds is

Osmic Anhydride or **Osmic Acid** : OsO_4, in which the metal is probably octavalent. This compound is produced when osmium is heated in a stream of oxygen, and is then deposited in

the cooler parts of the tube in colourless crystals. It is also obtained when the metal or its alloy, osmiridium, is heated in a stream of moist chlorine. The corresponding chloride, which is then presumedly first produced, but which is not known in the free state, is at once decomposed into osmic acid by the moisture of the damp gas. It melts under 100° to a colourless liquid, boils at a slightly higher temperature, and sublimes in colourless glistening needles. Osmic acid possesses a piercing odour, somewhat resembling chlorine, and powerfully attacks the lungs and eyes. Great care must therefore be exercised in experimenting with this substance. Osmic acid, or more correctly, osmic anhydride, dissolves in water, but a compound with this liquid, which would be the true osmic acid, has not yet been prepared. Most reducing substances separate metallic osmium from its solution, a change which also goes on when the liquid is exposed to the light. A dilute solution is used by biologists for hardening organic tissues.

Potassium Osmite: $K_2OsO_4 + 2H_2O$, separates, as a red crystalline powder, when alcohol is added to a solution of osmium tetroxide in caustic potash.

RUTHENIUM.

Chemical Symbol: Ru.—*Atomic Weight*: 101·4.

This metal, which resembles iridium and osmium, is less difficultly fusible than the latter, but more so than the former metal. It has a specific gravity of 12·3, is scarcely soluble in aqua regia and insoluble in other acids. When fused with caustic potash and nitre soluble *potassium ruthenate*: K_2RuO_4, is formed, and when chlorine is led into a solution of this salt the temperature becomes high enough to volatilize the oxide *ruthenic acid*: RuO_4, which is then formed. This compound then condenses in a cooled receiver as a yellow crystalline mass. In this respect, ruthenium resembles osmium, and the two metals are, at present, the only elements known of which one atom can unite with four atoms of oxygen.

APPENDIX.[1]

Atomic and Molecular Weights.

THE atomic weights of the elements play so important a part both in theoretical and in practical chemistry, that a brief account of the methods used to obtain these numbers may not be out of place, even in an elementary text-book of the science.

In deciding upon the number which shall be considered as the atomic weight of an element, two distinct questions must be experimentally answered. In the first place, the weight of the element must be found which unites with a given weight of some other element or elements, of which the atomic weight or weights are accurately known; and, secondly, it must be decided whether the number, so obtained, is really the atomic weight, or whether it is only some simple multiple or fraction of it. It is hardly necessary to remind the student that the atomic weights are simply relative and not absolute numbers, and that, since the atomic weight of hydrogen is taken as unity, the atomic weights of the *other elements simply express how much heavier their atoms are than those of* hydrogen.

The first thing to be done in determining the atomic weight of an element is, therefore, to find the ratio *(chemical equivalent)* in which it combines with other elements. For this purpose, the element is either made to unite with other elements of which the atomic weights are accurately known, or else one of its compounds with these elements is decomposed and its composition accurately determined. Such experiments appear simple enough theoretically, but in practice are surrounded by many and often almost insuperable difficulties if accurate results are to be obtained. The element or its compound must be prepared in a state of absolute purity, and only perfectly pure chemicals must be used in all succeeding operations. The greatest care must be taken that no impurities are introduced either from the air or from the vessels employed, and, what is more difficult to avoid, that a constant error does not occur through the entire series of experiments and so vitiate them all. To eliminate this constant error as far as possible, it is advisable to use not one but several compounds of the element for these determinations, and to employ material which has been obtained from various localities. The chemist must have an accurate balance

[1] By the Editor.

at his disposal, and must know how to use it properly; he must find beforehand whether his set of weights are exact ratios of one another, for example, whether the 10-gramme piece is exactly ten times as heavy as the 1-gramme, and one-tenth as heavy as the 100-gramme piece, and if they differ from this ratio, as the best weights always do, he must find how much they differ and make the necessary corrections in his weighings.[1] Finally, he must add to all his results the weight of air displaced by the substance weighed, which will vary according to the specific gravity of the substance, and according to the height of the barometer, the amount of moisture contained in the air and the temperature at the time of weighing.

The above brief description will give some idea of the delicacy of the operations which are necessary for a correct determination of the chemical equivalent of an element, and it may be safely affirmed that such investigations demand greater skill on the part of the operator than almost any other chemical experiments.

Supposing, then, that the ratio in which the element combines with other elements (or its equivalent) has been accurately determined, it remains to find its true atomic weight. Let us imagine, for example, that a given weight of pure carbon (the diamond) was burnt in a stream of pure oxygen, that the carbonic acid so produced was carefully collected and weighed by absorbing it in a series of potash-tubes, and that it was then found that 3·66 grammes of carbonic acid were produced for every gramme of carbon burnt. It would then be known that 1 gramme of carbon, when burning to carbonic acid, combines with $3·66 - 1·00 = 2·66$ grammes of oxygen, or that 6 grammes of carbon combine with 16 grammes of oxygen. If, then, the atomic weight of oxygen is 16, that of carbon must be 6, or some simple multiple of this number. It would be 6 if the compound contained an equal number of atoms of each constituent, 12 if it contained twice as many oxygen atoms as those of carbon, and 3 if twice as many carbon as oxygen atoms were present. Or, again, suppose that silicon chloride were decomposed in some suitable manner so that its chlorine was converted into silver chloride, and that, knowing the atomic weights of silver and chlorine and the composition of silver chloride, it was found that 100 grammes of silicon chloride contain 83·53 grammes of chlorine. Such a result would show that $100 - 83·53 = 16·47$ parts of silicon combine with 83·53 parts of chlorine, or that 7 parts of silicon unite with 35·5 parts (one atom) of chlorine. Hence the atomic weight of silicon might be 7 or 14 or 28 or 3·5. In order to decide which of these numbers correctly represents the atomic weight, further experiments are necessary and other considerations must be brought to bear on the problem. The further considerations which assist us in obtaining a solution of this question may be classified under three heads, viz. :—

1. The relations between the molecular weights of gases and their density (Avogadro's law);

2. The relations between the specific heats of the solid elements and their atomic weights (Dulong and Petit's law); and

3. The relations between the composition of a solid compound and its crystalline form (isomorphism).

Let us now see how we can use these three laws to fix the atomic weights of the elements.

I. *The determination of the atomic weight of an element from the density of its gaseous compounds.*

The important law, first enunciated by *Avogadro* and therefore called after him, states that equal volumes of all gases whether simple or compound contain an equal number of molecules, or, in other words, that the density of a gas is proportional to its molecular weight (see p. 50). Avogadro's law is proved not only because it agrees with all known chemical facts, but also because it explains the physical properties of gases in the only possible manner.

In the kinetic theory of gases, as worked out by Maxwell, Clausius, and others, it is supposed that a gas consists of a large number of small particles (molecules) moving at a high but variable velocity, and, therefore, constantly colliding with one another and with the walls of the vessel which contains the gas. This collision of the molecules with the walls of the vessel produces the pressure which the gas exerts, or the pressure which must be applied to the gas to prevent it from expanding. If, now, we call m the mass of each molecule and v the *mean* velocity with which the molecules are travelling, the *average* kinetic energy possessed by each molecule is : $\frac{1}{2} m v^2$. But if two substances are at the same temperature there is no change in the temperature of either when they are brought into contact with one another; there is, it is true, an interchange of heat between them, but each gains as much heat as the other loses. Hence, if two average molecules of the same or different gases at the same temperature are brought together, no change in their temperature is produced, and no change in their kinetic energy (measured as heat) takes place—*i.e.* the kinetic energy of each is equal, or :

$$\tfrac{1}{2} m_1 v_1^2 = \tfrac{1}{2} m_2 v_2^2.$$

Again, if u_1, u_2, u_3 be the mean velocities of molecules in three directions mutually at right angles, and if n be the number of molecules in unit volume, the pressures on the three planes perpendicular to the direction of the components of velocity will be respectively :

$$n\, m\, u_1^2,\ n\, m\, u_2^2,\ n\, m\, u_3^2.$$

As, in every gas at rest, the pressure, p, is equal in all directions, $u_1 = u_2 = u_3$. But $v^2 = u_1^2 + u_2^2 + u_3^2$. Hence $p = \frac{1}{3} n\, m\, v^2$. If the pressures of the gases are equal, $\frac{1}{3} n_1 m_1 v_1^2 = \frac{1}{3} n_2 m_2 v_2^2$.

But we have already seen (1) that at the same temperature, $\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2$. Therefore :—

$$n_1 = n_2,$$

or *the number of molecules contained in equal volumes of all gases at the same temperature and pressure is the same.*

Further, the density of a gas is clearly the product of the number of molecules contained in unit volume into the mass of each—*i.e.* $d_1 = n_1 m_1$ and $d_2 = n_2 m_2$, and since $n_1 = n_2$, we get :

$$d_1 : d_2 = m_1 : m_2.$$

or *the density of a gas is proportional to the mass of its molecules or its molecular weight.*[1]

This is a brief *résumé* of the physical proof of Avogadro's law with which we started.

It must now be decided with what standard the molecular weights are to be compared. We know by experiment that a given volume of oxygen, for example, weighs 16 times more than the same volume of hydrogen at the same temperature and under the same pressure, and, therefore, that the molecule of oxygen must be 16 times as heavy as the molecule of hydrogen, but we do not know how many atoms are contained in the molecule of each gas. That the molecule of hydrogen contains *at least* two atoms is clear from the following. In the union of hydrogen and chlorine equal volumes of the two gases combine to form the same volume of hydrochloric acid. Or, one molecule of hydrogen unites with one molecule of chlorine and produces two molecules of hydrochloric acid. Each molecule of hydrogen (and of chlorine) is therefore broken up into two parts which cannot be less than the atom, but *may* contain more than one atom. Hence, therefore, the molecule of hydrogen is considered to consist of 2 atoms; it is not impossible, but highly improbable, that its molecule may contain some multiple of this number of atoms.

The atomic weight of hydrogen being taken as unity, and its molecule consisting of 2 atoms, its molecular weight becomes 2. And since air is 14·44 times as heavy as hydrogen, the molecular weight of any gas is found by multiplying its density (compared with air as unity) by $2 \times 14 \cdot 44 = 28 \cdot 88$ (p. 15). In this way the molecular weights of a number of the elements and of many compounds have been determined. But in making these determinations our experiments are confined to those substances which are volatile at comparatively low temperatures; and, in the case of a compound, to those which do not completely decompose when heated above their boiling-point, or which do not *dissociate* or decompose when heated, and recombine again on cooling. And, from the experimental difficulties which surround the determination of many vapour densities as well as the deviation from Boyle's and Charles' laws at temperatures only slightly above the boiling-point of a substance, it follows that the molecular weights obtained in this way are never so correct as those derived from the ordinary analysis of the substance. The density of the gas only tells us whether the molecular weight is a multiple or fraction of a certain number, and does not give us the exact number itself. We have seen (p. 574) that, by chemical analysis, silicon chloride contains 7 parts of silicon united with 35·5 parts of chlorine, and its molecular weight is therefore either 42·5 or some exact multiple of this. The density of this gaseous compound has been found to be 5·94, which, when multiplied by 28·88, gives 171·5, consequently its true molecular weight is $42 \cdot 5 \times 4 = 170 \cdot 0$, not 171·5, nor any other multiple of 42·5.

The following table gives the vapour densities (*d*) of those of the elements for which this has been determined; the third column contains the molecular weight (28·88*d*) to which this points; and the fourth the true molecular weight (*M*):—

[1] Maxwell, *Theory of Heat*, pp. 289 *et seq.*

Element	d	$8 \cdot 88 \times d$	M
Hydrogen	0·0693	2·00	$H_2 = 2$
Oxygen	1·1056	31·93	$O_2 = 32$
Nitrogen	0·9-13	28·05	$N_2 = 28$
Chlorine	2·45	70·75	$Cl_2 = 71$
Bromine	5·54	160·00	$Br_2 = 160$
Iodine	8·72	251·8	$I_2 = 254$
Selenium (at 1,400°)	5·68	164·0	$Se_2 = 158$
Sulphur (at 1,000°)	2·24	64·7	$S_2 = 64$
„ (at 500°)	6·78	195·8	$S_6 = 192$
Tellurium	9·08	262·2	$Te_2 = 256$
Mercury	6·99	201·8	$Hg = 200$
Cadmium	3·94	113·8	$Cd = 112$
Phosphorus	4·48	129·4	$P_4 = 124$
Arsenic	10·42	300·9	$As_4 = 300$
Zinc	2·38	68·7	$Zn = 65$

From this table it will be seen that the majority of the elements contain two atoms in the molecule. To this rule, the hexatomic sulphur, at temperatures *just above its boiling point, forms an exception, as well as the five elements*—mercury, zinc, cadmium, phosphorus, and arsenic. The molecules of mercury, zinc, and cadmium are monatomic, an assumption which is strongly supported in the case of mercury by certain physical properties of its gas; while the molecules of phosphorus and arsenic are made up of four atoms each.[1]

We possess, then, in Avogadro's law a valuable and certain means for finding the molecular weights of substances which can be converted into the gaseous state without decomposition;[2] but it remains to be seen how we can utilize the *same generalization for determining the atomic weight of an element.* In the first place, it is evident from the preceding table that the molecular weight of an element has no definite relation to its atomic weight, and we are not therefore justified in making any deduction from the molecular weight of an element as to its atomic weight. But the true atomic weight of an element may often be found from the molecular weights of its compounds. The atom of an element may be defined as the smallest quantity which can exist in any compound, and among a large number of compounds of one element it is extremely probable that the molecule of one or more of them will contain only one atom. If, therefore, we have determined the vapour densities, and consequently the molecular weights, of a number of compounds of one particular element, we may take the atomic weight as the *smallest* quantity of the element which occurs in the molecule of any of these compounds. The result so obtained is never absolutely certain, because a compound might be discovered containing a less quantity of the element than its received atomic weight, and it has but little value when the number of compounds compared together is small, but approaches certainty when the densities of a large number of compounds are

1 Chlorine, bromine, iodine, phosphorus, and arsenic dissociate at high temperatures, like sulphur, into simpler molecules.

2 See note on Raoult's method of determining molecular weights—p. 594.

known. The number obtained from this comparison is the *maximum* value possible for the atomic weight—it may be smaller, but it cannot be larger.

A few examples may serve to explain more clearly how the atomic weight of an element may thus be found. Among those elements of which numerous gaseous compounds are known is chlorine. If we examine all these compounds, we find that none of them contains less than 35·5 parts of chlorine in its molecule, and we therefore consider this number as the atomic weight of the element.

The following table gives the percentage composition of four compounds of chlorine, their vapour density (d), the molecular weight indicated by this density ($28·88 \times d$), and the true molecular composition (M):—

Compound	Percentage composition	d	$28·88 \times d$	M
Hydrochloric acid .	H = 2·74 Cl = 97·26	1·247	36·0	H = 1·0 C = 35·5
Mercuric chloride .	Hg = 73·80 Cl = 26·20	9·80	283·0	Hg = 200 Cl = 71 = 35½ × 2
Phosphorous chloride	P = 22·56 Cl = 77·44	4·88	140·9	P = 31 Cl = 106·5 = 35½ × 3
Silicon chloride .	Si = 16·47 Cl = 83·53	5·94	171·6	Si = 28 Cl = 142 = 35½ × 4

The table shows that the chlorine contained in the molecules of the four compounds is in the proportion of 1 : 2 : 3 : 4, and as on examining a large number of other compounds of the element none has been found with less chlorine in its molecule than hydrochloric acid, we consider that this compound contains one atom of chlorine, mercuric chloride two atoms, &c. At present, therefore, the atomic weight of chlorine is taken as 35·5, but if, at any future time, a compound of chlorine should be discovered with only 17·75 parts of chlorine in its molecule, the present atomic weight would have to be reduced to this number. In the same way, from the comparison of a still larger number of vapour densities, the atomic weight of carbon has been fixed at 12, and that of oxygen at 16. And the corresponding numbers for many other elements have been determined with more or less certainty, according to the number of compounds examined.

The atomic weights obtained from Avogadro's law are increased in value by their agreement with those resulting from other considerations. They agree with those derived from the specific heats of the elements in the solid state, and from the general properties of the element and its compounds.

II. *The determination of the atomic weight of an element from its specific heat in the solid state.*

The specific heat of a substance is the quantity of heat required to raise 1 gramme of the substance 1° C. as compared with the quantity of heat required to raise 1 gramme of water through the same increment of temperature. The specific heats (or capacities for heat) of the various elements differ very considerably from one another. But if, instead of comparing together the quantities of heat required to raise *equal weights* of the elements 1°, we compare those necessary to similarly increase the temperature of the *atomic weights* of the elements (in the solid state), we arrive at a different result: we then find that all these quantities of heat are nearly equal to one another. This important law, to

which we have already referred (p. 70), was discovered by *Dulong* and *Petit*, and is therefore usually named after them. The law may also be expressed by saying that the capacity for heat of all the elementary atoms in the solid state (*atomic heat*) is the same, or, that the product of the specific heat of a solid element and its atomic weight is a constant. The following table gives the specific heats of some of the elements in the solid state (*s*), the temperature (*t*) at which these quantities have been determined, the atomic weights (*a. w.*) of these elements and their atomic heats (*a. h.*); or the product of the specific heat and atomic weight in each case :—

Element	*s*	*t*	*a. w.*	*a. h.*
Lithium	0·941	64°	7·0	6·6
Boron	0·366	233	11·0	4·0
Carbon (Diamond)	0·459	985	12·0	5·5
Silicon	0·203	232	28·0	5·7
Phosphorus	0·189	19	31·0	5·9
Sulphur	0·171	50	32·0	5·5
Potassium	0·166	−34	39·0	6·5
Iron	0·112	+31	56·0	6·3
Copper	0·095	58	63·4	6·0
Silver	0·056	50	108·0	6·0
Tin	0·056	50	118·0	6·6
Platinum	0·0324	55	198·0	6·4
Lead	0·0315	55	207·0	6·5

This table shows us, in the first place, that the atomic heats of the very various elements which it includes are all approximately equal, but we also see that the numbers differ considerably among themselves. These differences are principally due to the change of specific heat with temperature, which nearly always increases as the temperature rises. The most striking examples of this are seen in the elements carbon, boron, and silicon. At the ordinary temperatures the specific heats of these three substances are :—

Carbon = 0·132 (at 33°)
Boron = 0·238 (at 26°)
Silicon = 0·170 (at 22°)

numbers which do not at all agree with the law—*e.g.* the atomic heat of carbon is then $0·132 \times 12 = 1·58$. But as the temperature rises the specific heat of each rapidly increases until it becomes, to a certain extent, constant, and the atomic heat is then found to be normal. Thus, at high temperatures, the three elements have the following specific heats :—

Carbon = 0·459 (at 985°)
Boron = 0·366 (at 233°)
Silicon = 0·203 (at 232°)

For carbon and silicon these numbers correspond to the normal atomic heat, and that for boron probably would do so at a slightly higher temperature.

Dulong and Petit's law is therefore only approximately true, or the specific

heat is a function not only of the atomic weight, but also of other properties of solids with which we are at present but little acquainted. But notwithstanding this, the law enables us to decide between one of two or more numbers, differing considerably from one another, in determining the atomic weight of an element. *All that is necessary to find the required atomic weight is to divide the mean atomic heat (6·4) by the specific heat of the element in the solid state.* The quotient is then the approximate atomic weight, which has to be corrected by ordinary analytical results. An example may be given of how the specific heat of a solid element controls its atomic weight. When the metal indium was discovered by spectrum analysis it was found in association with zinc, a metal which it closely resembles both in the free state and in its compounds. The only oxide which indium forms was therefore thought to correspond to the only oxide of zinc—*i.e.* to be a monoxide of the formula: InO; and this gave an atomic weight of 75·6. But soon afterwards the specific heat of the metal was determined and was found to be 0·057, which gives an approximate atomic weight of $\frac{6·4}{0·057} = 112$, and hence its true atomic weight is, not 75·6, but $75·6 \times 1·5 = 113·4$. From this it also follows that the formula of its oxide becomes In_2O_3, and that the composition of all its other compounds must be correspondingly changed. Two atoms of indium now correspond to three of what were formerly considered as the atoms of the element.

III. *The determination of the atomic weight of an element from the crystalline form of its solid compounds.*

It was discovered by Mitscherlich that many substances which crystallize in the same form with the same or nearly the same angles have a similar chemical composition. Such substances are said to be *isomorphous* with one another, and this law of isomorphism may be used to determine the atomic weight of an element in the following way. *If two substances crystallize in the same form and the composition of one is known, the composition of the other may be inferred to be similar*, and thus the atomic weight of any particular element which it contains may be fixed. The compounds alumina, ferric oxide, and chromic oxide all crystallize in the same form of the hexagonal system, and from the composition of one of them we can therefore deduce that of the other two: if ferric oxide $= Fe_2O_3$, then alumina $= Al_2O_3$, and chromic oxide $= Cr_2O_3$; and from this ratio the atomic weights of aluminium and chromium may be deduced if that of iron is known.

The atomic weights obtained by isomorphism are not, however, so trustworthy as those based upon Avogadro's or Dulong and Petit's law, and for the following reasons. That the form in which a substance crystallizes does not *entirely* depend upon its chemical composition is at once proved by the fact that the same compound may be *dimorphous*, or may crystallize in two distinct and entirely different forms—*e.g.* calcium carbonate, arsenious anhydride, sulphur, &c. In the next place, the composition of two compounds may be exactly similar, but they *need not* crystallize in the same form—*e.g.* the nitrates and the corresponding metaphosphates. And, finally, two substances may crystallize in precisely the same form without having a similar composition—*e.g.*

sodium nitrate ($NaNO_3$) and calcite ($CaCO_3$); sodium sulphate (Na_2SO_4), and barium permanganate (BaM_2O_8); cadmium sulphate ($3CdSO_4 + 8H_2O$), and didymium sulphate ($Di_23SO_4 + 8H_2O$).[1] The evidence derived from isomorphism is, therefore, only of value so far as it *confirms the results derived from* the other two laws, or when these two laws cannot be applied. Thus the isomorphism of the compounds :—

$$K_2SiF_6 + H_2O$$
$$K_2TiF_6 + H_2O$$
$$K_2ZrF_6 + H_2O$$
$$K_2SnF_6 + H_2O$$

afforded valuable evidence concerning atomic weights of silicon, titanium, and zirconium, until they were confirmed by the other two more certain laws.

The following is a list of some of the more important isomorphous groups, showing the chief elements which are connected together by this law :—

Groups.	*Elements Connected.*
(i.) Phosphates Arsenates	P and As
(ii.) Carbonates of the composition : RCO_3, where R = Ca, Mg, Fe,″ Zn, Mn.	Ca, Mg, Zn, Fe, Mn
(iii.) Double sulphates of the general formula: $M'_2SO_4 + M''SO_4 + 6H_2O$, where M′ = K, NH_4 M″ = Fe″, Co, Ni, Mg, Zn, Cd, Mn″	Fe″, Co, Ni, Zn, Mg, Cd, Mn″
(iv.) The Alums of the general formula: $M'M'''2SO_4 + 12H_2O$, where M′ = K, NH_4, Rb, Cs, Na, Tl, Ag M‴ = Al, Fe‴, Mn‴ Cr‴	K, (NH_4), Rb, Cs, Na, Tl, Ag Al, Fe‴, Mn‴, Cr‴
(v.) Chromates, Manganates, Sulphates, and Selenates	Cr^{vi}, Mn^{vi}, S, Se,
(vi.) $KMnO_4$ and $KClO_4$	Mn^{vii}, Cl^{vii}
(vii.) Ag_2SO_4, Na_2SO_4	Ag, Na
(viii.) K_2SiF_6, H_2O; K_2TiF_6, H_2O; K_2ZrF_6, H_2O; K_2SnF_6, H_2O.	Si, Ti, Zr, Sn
(ix.) Apatite : $3Ca_3P_2O_8$, $Ca(Cl, F)_2$ Pyromorphite : $3Pb_3P_2O_8, PbCl_2$ Mimetesite : $3Pb_3As_2O_8, PbCl_2$ Vanadinite : $3Pb_3V_2O_8, PbCl_2$	P, As, V Pb, Ca

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1 Kopp's modification of Mitscherlich's law—viz. that substances which are capable of *crystallizing upon one another without changing the form of the original crystals* possess similar chemical constitution—is more reliable; but few substances only have as yet been shown to be, according to this stricter test, isomorphous.

Relations between the Atomic Weights.

It has been already remarked (pp. 65 *et seq.*) that certain of the elements which possess similar chemical properties and which usually occur associated together in nature may be arranged in groups of three; and that when this is done the atomic weight of one is about the mean of the other two. The following have been mentioned as examples of this triple grouping:—

(i.)	Chlorine	=	35·5	Mean	= 81·25
	Bromine	=	80·0		
	Iodine	=	127·0		
(ii.)	Sulphur	=	32·0	Mean	= 80·0
	Selenium	=	79·0		
	Tellurium	=	128·0		
(iii.)	Lithium	=	7·0	Mean	= 23·0
	Sodium	=	23·0		
	Potassium	=	39·0		

These relations cannot be accidental, and it certainly does appear that the properties of an element and of its compounds are related in some way or other to its atomic weight.

Of the various numerical relations which have been supposed to exist between the atomic weights we shall here only refer to one hypothesis, which was put forward by Prout, and is commonly known as *Prout's law*. With regard to the connexion between the atomic weight of an element and its properties, the most important theory is that known as the *Periodic law*. This theory, which has been developed in late years by Newlands, Lothar Meyer, and Mendelejeff, supposes that the properties of the elements change *periodically* as we pass from one to the other when arranged according to their atomic weights.

Prout's Law.—The hypothesis which is known under this name supposes that the atomic weights are all multiples of that of hydrogen by whole numbers, and that the elements may therefore be considered as compounds of hydrogen of varying degrees of complexity. Prout's hypothesis was advanced at a time (1815) when the atomic weights were much less accurately known than they are at present, and when they were usually represented by the nearest whole numbers to which the results pointed. It soon became clear, however, that the atomic weights of certain of the elements, notably chlorine, could not be represented by whole numbers, and in order to make the hypothesis applicable to these it was proposed to call the atomic weight of hydrogen 2, or even 4. But even with such devices as this, accurate determinations of the atomic weights of many of the elements by which every possible error was avoided or allowed for have shown that in most cases the hypothesis is certainly not true.

The atomic weights which are given on p. 60, and used in the text of this book, have been mostly taken as whole numbers to avoid fractions; but for some elements much more accurate results than this have been obtained by careful investigators and have been confirmed by others. The following table

gives a list of these more accurate atomic weights, which shows that only in a few cases is Prout's hypothesis approximately true. In the second column the ratio between the atomic weights of hydrogen and oxygen is 1 : 15·96, and in this column the atomic weights are calculated for these numbers. We may, however, consider the atomic weight of oxygen as 16, when all the other atomic weights will be slightly larger. These numbers are given in the third column. It will be noticed that the atomic weights there more nearly approach whole numbers, and hence Prout's law has not yet been completely forsaken by some chemists.

Table of Accurately Determined Atomic Weights.

Element	O = 15·96	O = 16
Aluminium	27·02	27·09
Antimony	119·8	120·1
Barium	136·81	137·15
Boron	10·92	10·95
Bromine	79·76	79·96
Cadmium	111·75	112·03
Cæsium	132·65	132·98
Calcium	39·95	40·05
Carbon	11·97	12·00
Chlorine	35·37	35·46
Copper	63·18	63·34
Hydrogen	1·00	1·0025
Indium	113·4	113·7
Iodine	126·55	126·87
Iridium	192·5	192·98
Iron	55·9	56·14
Lead	206·43	206·95
Lithium	7·01	7·03
Mercury	199·7	200·8
Nitrogen	14·01	14·05
Oxygen	15·96	16·00
Phosphorus	30·96	31·03
Platinum	194·3	194·79
Potassium	39·02	39·12
Rubidium	85·2	85·4
Selenium	78·8	79·0
Silver	107·67	107·94
Sodium	22·99	23·05
Strontium	87·3	87·5
Sulphur	31·98	32·06
Vanadium	51·1	51·2

The Periodic Law.

If the elements are arranged according to their atomic weights, commencing with the smallest, it is found that those elements with similar chemical and physical properties occur at regular intervals. Various tables have been drawn up to exhibit these periodic changes in the properties of the elements, one of which

is given below, and the series of facts thus shown to be connected with the atomic weight are collectively known as the periodic law. We owe this useful generalization principally to the labours of Lothar Meyer and Mendelejeff :—

I	II	III	IV	V	VI	VII	VIII		
H 1									
Li 7	Be 9	B 11	C 12	N 14	O 16	F 19			
Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35·5			
K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 59
[Cu] 63	Zn 65	Ga 70	Ge 72	As 75	Se 79	Br 80			
Rb 85	Sr 88	Y 89	Zr 90	Nb 94	Mo 96		Ru 101	Rh 103	Pd 106
[Ag] 108	Cd 112	In 113	Sn 118	Sb 120	Te 126	I 127			
Cs 133	Ba 137	La 139 (?)	Ce 141	Di 145 (?)					
		Er 166	Yb 173	Ta 182	W 184		Os 190	Ir 193	Pt 194
[Au] 197	Hg 200	Tl 204	Pb 207	Bi 210					
			Th 233		U 240				

Referring to the accompanying table, which commences with hydrogen and ends with uranium, we find that, omitting hydrogen, the first seven elements correspond in their properties to the next following seven : thus, Li corresponds to Na, C to Si, N to P, &c. Following on in the series we see again that the next seven also correspond in a regular manner to the preceding seven. In this way the elements become classified into various groups, which are shown in the vertical columns of the table, and which contain closely related elements. Group I., for example, contains Li, Na, K, Rb, Cs, and the allied metals Ag and Cu, as a sub-group ; Group II. includes the metals of the alkaline earths, together with Zn, Cd, and Hg. The elements in each of these groups are not only allied chemically but also often connected by similar physical properties ; they further possess the same atomicity in some of their

compounds. The elements included in the first group are monads, those in the second group are diads, and so on.

This brief description of the periodic law, which space does not allow us to expand more fully, shows clearly that the properties possessed by an element are closely connected with its atomic weight; and that the method in which the elements are arranged is to some extent correct, is corroborated by other considerations.* It will be noticed that there are several gaps in the above table—*e.g.* between Mo and Ru, and a large number among the elements of higher atomic weights. These gaps are supposed to be occupied by undiscovered elements, a supposition which received a remarkable confirmation in the recent discovery of the metal germanium. Mendelejeff had previously predicted that such a metal might exist, and had described its properties and approximate atomic weight under the name of *ekasilicon.* And when many years afterwards the metal now called germanium was discovered, its properties were found to agree almost exactly with Mendelejeff's hypothetical ekasilicon. The periodic law has also done good service in correcting some uncertain atomic weights. Comparatively recently the metals of the cerium and yttrium groups were considered as diads and their oxides as monoxides; but Mendelejeff showed that the atomic weights which they then possessed did not agree with their properties according to the periodic law, and proposed to multiply these numbers by 1·5, so that the oxides would become sesquioxides. The atomic weights which he had proposed for the cerium metals were afterwards found to be correct as soon as their specific heats were determined. In the same way the atomic weight of uranium was formerly thought to be 120, but was supposed by Mendelejeff to be 240—a supposition which was also confirmed by a determination of the specific heat of the metal.

NOTES.

Page 6.—Water *has* been decomposed at a very high temperature, as when molten platinum has been poured into it. According to St. Claire Deville, decomposition commences at 1200° but is not completed until a temperature of 2500° is reached.

Probably every compound would be decomposed if heated to a sufficiently high temperature: but the dissociation temperatures of most compounds cannot as yet be practically attained. There are two other practical difficulties in determining by the use of heat alone the composition of a compound, even when decomposed at a low temperature: (i.) the constituent elements may reunite on cooling, and (ii.) it may not be possible to separate them even when set free and thus to recognise them. In order to effect this they should volatilise with different degrees of readiness.

Page 19.—Hydrogen forms one of the principal constituents of the so-called 'water-gas.' This is produced by passing steam over strongly heated coke. The principal reaction that takes place is represented by the following equation:—

$$H_2O + C = CO + H_2.$$

The gas evolved, which is inflammable and burns with evolution of great heat, is thus mainly a mixture of hydrogen and carbon monoxide.

Page 56.—It has been suggested by the Committee of Publication of 'The Journal of the Chemical Society' that these compounds should be invariably called hydroxides, 'the term hydrate being reserved for compounds supposed to contain water of combination or of crystallization.'

Page 76.—100 parts water dissolve at 14° and 100° respectively, 35·87 and 39·16 parts of common salt.

Page 90.—Hydrogen peroxide may also be prepared from barium peroxide, and the barium precipitated and thus separated from the hydroxyl formed, by the use of other reagents, *e.g.* hydrofluosilicic acid and carbonic acid:

$$BaO_2 + H_2SiF_6 = BaSiF_6 + H_2O_2.$$
$$BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2.$$

Page 95.—A thin glass bulb containing a solution of potassium iodide is introduced into a glass tube closed at one end; the tube is filled with pure dry oxygen, and its open end is connected with a pressure-gauge. On passing a silent discharge of electricity through the oxygen, a contraction is observed; some of the oxygen is converted into ozone, and the volume of the gas becomes

smaller. Suppose the contraction to be 20 c.c.; the weight of iodine liberated will then be found to be 455 milligrammes. This weight corresponds to 28·67 mgr. of nascent oxygen, for (127 × 2) mgr. of iodine require 16 mgr. of oxygen to liberate it from potassium iodide, according to the equation

$$2KI + H_2O + O = 2KOH + I_2.$$

Now 28·67 mgr. is the weight of 20 c.c. of oxygen. Hence the contraction which occurs on the formation of ozone is equal to the volume of oxygen used in oxidation when ozone is brought into contact with a reducing body and becomes converted into oxygen, the volume of the gas in the tube remaining unchanged. These facts are best explained by the supposition that the molecule of ozone contains three atoms, while the molecule of oxygen contains two.

The molecular formula for ozone is further established by comparing the rate of diffusion of a mixture of ozone and oxygen with that of a mixture of chlorine and oxygen. The rate of diffusion of two gases is, as was shown by Graham, *inversely proportional to the square roots of the respective densities.* The density ($H = 1$) of ozone was thus shown to be 24, giving a molecular weight of 48, i.e. corresponding to the molecular formula: O_3.

Page 98.—The reaction is more complete if the bricks be first soaked in a saturated solution of cupric sulphate, and advantage is taken of this fact in the actual manufacture, though the precise part played by the copper salt has not been definitely determined.

Page 111 (i.).—Potassium chlorate is now more generally manufactured by the following method: Chlorine is passed into hot milk of lime, which undergoes a similar decomposition to caustic potash, the hypochlorite, if momentarily formed, being decomposed into chlorate, so that the completed reaction may be represented thus:—

$$6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca2ClO_3 + 6H_2O.$$

After the excess of lime-mud has settled, the supernatant liquid is drawn off and heated with a solution of potassium chloride, now obtained in large quantity from Stassfurt, and which is added in quantity sufficient to decompose all the calcium chlorate present.

$$5CaCl_2 + Ca2ClO_3 + 2KCl = 2KClO_3 + 6CaCl_2.$$

All the potassium present is thus converted into potassium chlorate, which crystallizes out and is purified by recrystallization from hot water.

Page 111 (ii.).—The equation representing the decomposition of potassium chlorate by heat probably more closely approximates to

$$8KClO_3 = 5KClO_4 + 3KCl + 2O_2.$$

The proportion of perchlorate to chloride formed appears, however, to vary with the temperature.

Page 114.—The existence of Cl_2O_3 is very doubtful. Probably the substance whose preparation and properties are described on pages 114 and 115 is a mixture of chlorine and chlorine peroxide.

Page 124.—The density of iodine vapour diminishes with increasing temperature and, at about 1,500°, is only 5·06. This is accounted for by the gradual decomposition of the original diatomic molecules into monatomic molecules. This dissociation would doubtless become complete at a still higher temperature.

Page 127.—Some hydriodic acid is formed when hydrogen and iodine are passed in the gaseous state over heated platinum-sponge.

Page 150.—When sulphur burns in air or oxygen, the volume decreases slightly, instead of remaining constant (as stated in the text). The contraction is due to the sulphuric anhydride which is always produced at the same time as the sulphurous anhydride. This is shown by the white fumes which always accompany the combustion.

Page 155.—In determining the composition of hyposulphurous acid, Schützenberger used potassium permanganate to oxidize the sulphur, and to discover in what form of oxidation it was contained in the compound. He obtained the formula $HSHO_2$, which represents a monobasic acid, and corresponds to an unknown oxide of sulphur, viz. SO. Bernthsen subsequentl showed that this formula does not represent the composition of the acid. He proved that Schützenberger's experiments were inexact, and also that potassium permanganate should not be used for such determinations as these.

Bernthsen is of opinion that this acid has really the composition $H_2S_2O_4$ or HSO_2, and that its anhydride is not SO $[SO + H_2O = H_2SO_2]$, but S_2O_3 $[S_2O_3 + H_2O = H_2S_2O_4]$. If this be correct, it follows that for every molecule of sulphur (S_2) contained in the acid we should require three molecules of iodine ($3I_2$) or three atoms of oxygen (3O) in order to oxidize it to sulphuric acid, according to the equations

$$S_2O_3 + 3O = 2SO_3$$
$$\text{or } H_2S_2O_4 + H_2O + 3O = 2H_2SO_4.$$

Again, for every molecule of sulphur contained in the acid, one atom of oxygen would be required in order to oxidize it to sulphurous acid :—

$$S_2O_3 + O = 2SO_2$$
$$\text{or } H_2S_2O_4 + H_2O + O = 2H_2SO_3.$$

The oxidation in the latter case could be carried out by means of copper sulphate, and two molecules of $CuSO_4$ would be required for the purpose.

Bernthsen has shown by a series of careful experiments that these conclusions are correct.

Page 157.—It is held by some chemists that N_2O_3, not NO, is the principal carrier of oxygen in the manufacture of sulphuric acid, the primary reactions taking place being represented as follows :

$$2SO_2 + 2NO_2OH + H_2O = 2SO_2\begin{cases}OH\\OH\end{cases} + N_2O_3.$$
$$N_2O_3 + O = N_2O_4$$
$$SO_2 + N_2O_4 + H_2O = SO_2\begin{cases}OH\\OH\end{cases} + N_2O_3.$$

N_2O_3 is however a very unstable substance, readily decomposing into nitric

oxide and nitric peroxide, and is probably incapable of existence as such at the temperature of the vitriol-chambers.

Page 159.—To obtain anhydrous sulphuric acid :—Distil the rectified acid, reject the first third of the distillate, and place the remainder in a freezing mixture. Crystals, which melt at 10·5° and consist of the dry acid, then separate.

Page 172.—*The action of* H_2S *upon an aqueous solution of* SO_2 *is actually* more complicated than that represented by the equation on page 172; for the solution ('Wackenroder's Solution') obtained was shown in 1888 by Debus to contain not only pentathionic acid and sulphur, the latter in two forms, one colloidal in solution, and one as oily drops in suspension, but also sulphuric *acid, a trace of trithionic acid, tetrathionic acid, and also a higher sulphur-acid,* probably hexathionic acid. A potassium pentathionate, $2K_2S_5O_6{\cdot}3H_2O$, was obtained from this complex solution by addition of potassium acetate, and careful recrystallization from water at 50°.

Page 178.—On cooling a solution of selenic acid of the requisite strength to 32°, crystals, which melt at 25°, of $H_2SeO_4{\cdot}H_2O$ are deposited.

Page 179.—*According to the experiments described by Brauner and Grün*wald in 1839 and 1890 respectively, it is probable that the substance ordinarily called tellurium is not a homogeneous element. The atomic weight, 127·6, is abnormal, as tellurium should, in order to take its proper place in Mendelejeff's periodic system (see page 584), possess an atomic weight between that of *antimony (119·96) and that of iodine (126·86).*

Page 197.—The substance thus described as nitryl chloride has been said to consist merely of a solution of chlorine in nitrogen peroxide.

Page 199.—An acid possessing the empirical formula HNO, although not directly obtainable by the union of N_2O and H_2O, has been prepared. A solution of KNO_3 is reduced by sodium-amalgam to KNO, from which the *corresponding silver salt, AgNO, is precipitated by treatment with silver* nitrate. The precipitate is decomposed by HCl, when silver chloride, AgCl, is precipitated, and *hyponitrous acid*, (?)HNO, is obtained in solution. This solution is colourless, possesses powerful reducing properties, and when heated with concentrated sulphuric acid or even alone, gives off N_2O.

Page 209.—*If, before distillation, the calcium metaphosphate be mixed with* *sand as well as with charcoal, all the phosphorus present is set free:*

$$Ca_2PO_3 + 5C + SiO_2 = CaSiO_3 + 5CO + P_2.$$

Page 210.—The dangerous practice here mentioned is now avoided, the liquid phosphorus being caused, without applying suction, to flow into the moulding tubes.

Page 214.—The oxide having the formula P_2O_4 is said to be formed by *burning phosphorus in a slow current of air and then distilling in vacuo.* An oxide whose composition would be represented by P_4O, and of which no nitrogen-analogue exists, is also said to have been prepared.

Page 215.—Graham stated that no such intermediate formation of $H_4P_2O_7$ takes place.

Page 217.—By treating bone-ash for a sufficient length of time with sulphuric

acid, the superphosphate at first formed is decomposed by that acid, the calcium being precipitated as sulphate, and phosphoric acid remaining in solution:

$$H_2SO_4 + Ca\begin{cases} H_2PO_4 \\ H_2PO_4 \end{cases} = CaSO_4 + 2H_3PO_4.$$

Page 220.—Hypophosphoric acid is separated from phosphorus and phosphoric acids by the sparing solubility of its di-sodium salt. This is then converted into the corresponding barium compound and the latter decomposed by sulphuric acid. On evaporating the filtrate in vacuo crystals of $H_4P_2O_6 \cdot 2H_2O$ separate.

Page 244.—Detection of arsenic:

(i.) Instead of using zinc in Marsh's apparatus, it is better to employ re-distilled magnesium. This metal can be obtained in commerce absolutely free from arsenic.

(ii.) *Reinsch's Test.*—This is a simple method for detecting arsenic in wall paper, wearing apparel, &c., and is so called after its discoverer. A portion of the substance to be examined for arsenic is cut up into small pieces and placed in a test-tube with a little hydrochloric acid and a small coil of bright copper foil. The tube is then gently warmed, when the arsenic (if present) dissolves in the liquid, and is reduced by the bright copper and deposited upon it. The copper is removed from the tube, gently washed with water, and dried between blotting-paper; if a sufficient quantity of arsenic be present, the copper will have become of a grey colour. It is now introduced into a clean dry test-tube and gently heated, when the arsenic volatilizes and is, for the most part, oxidized to arsenious anhydride. This can be examined for arsenic by any of the methods mentioned in the text.

Page 261.—According to Hampe all the crystals obtained by this process contain aluminium, and some contain also carbon.

Page 265.—Landolph states that he has, by the action of boron fluoride upon an organic compound (anethol), isolated fluoboric acid and that it is a colourless liquid boiling, with partial decomposition, at 130°.

Page 268.—SiO is said to have been obtained as one of the products of the action of heat upon silica when placed in a Cowles' electrical furnace lined with charcoal.

Page 271.—Serpentine and many other naturally occurring silicates may be looked upon as derived from hypothetical polysilicic acids produced by condensation, attended by separation of water, of molecules of $Si(OH)_4$. Thus $Mg_3Si_2O_7$ would be the Magnesium salt of the acid $H_6Si_2O_7$ ($2H_4SiO_4$ minus H_2O). Orthoclase, $KALSi_3O_8$, would be the double potassium and aluminium salt of the acid $H_4Si_3O_8$ ($3H_4SiO_4$ minus $4H_2O$).

Page 278.—It has been stated that diamond, in the form of microscopic crystals, has been obtained from a solution of carbon in molten silver.

Page 295.—Carbon monoxide has been liquefied by cooling it to −136° at a pressure of 200 to 300 atmospheres, and then diminishing the pressure. By the evaporation of a portion, the remainder may be converted into a snow-white, solid mass, which melts at −199°.

Page 304.—*Coal-mine explosions.* A mixture of methane with an excess of air explodes violently when ignited, and produces 'after-damp,' or carbonic

acid. This compound does not support respiration, and miners imprisoned in mines after explosions are suffocated by it. If dry coal-dust is present in the mine, it may, during the explosion, reduce the carbonic acid to carbon monoxide. This latter gas is a deadly poison (p. 295), a few whiffs causing instant death by displacing the oxygen in the blood. It has recently been shown that explosions may be propagated in air containing dry coal dust, without any methane. From these statements it will be seen how necessary it is to ventilate mines thoroughly in order to remove explosive gases, and to water the workings so as to wet and lay the coal-dust.

Page 305.—*Synthetical production of Methane.* Methane can be prepared synthetically by passing a mixture of carbon disulphide and sulphuretted hydrogen over red-hot copper turnings. The sulphuretted hydrogen is led through slightly warmed carbon disulphide, and the mixture of the two substances, in the gaseous state, is passed over the red-hot copper. The sulphur of both compounds combines with the metal, and the carbon and hydrogen combine with one another. The following equation shows the reaction :—

$$CS_2 + 2H_2S + 8Cu = 4Cu_2S + CH_4.$$

Page 307 note (i.)—This reaction takes place actually in two stages. In the cold there is formed hydrogen ethyl sulphate, which, on the subsequent application of heat, is decomposed with evolution of ethylene :—

$$C_2H_5OH + H_2SO_4 = \left.\begin{matrix} H \\ C_2H_5 \end{matrix}\right\} SO_4 + H_2O$$

$$HC_2H_5SO_4 = C_2H_4 + H_2SO_4.$$

Thus the sulphuric acid is regenerated and *appears* to have remained unchanged.

Page 307 note (ii.)—*Synthesis of Ethylene* : C_2H_4. If an electric arc is formed between carbon poles in an atmosphere of hydrogen, the carbon unites with the hydrogen, forming acetylene : C_2H_2. It combines with a further quantity of hydrogen and produces ethylene : C_2H_4. Both these gases burn in air, and are among the illuminating constituents of coal-gas.

Page 336.—The anomaly is avoided by speaking of 'hydrogen,' instead of 'acid' salts. Thus: dihydrogen potassium phosphate, hydrogen dipotassium phosphate (and normal, not neutral, potassium phosphate). This system of nomenclature is now more frequently adopted.

Page 364.—The product of the action of heat upon a mixture of potassium carbonate and sulphur seems to vary with the relative proportions in which these substances are mixed and with the temperature to which the mixtures are heated. Thus the sesquisulphide, K_2S_3, has been found to be the principal constituent of some preparations of liver of sulphur.

Page 367.—Sodium sulphate is prepared, also upon a large scale, by passing steam, sulphur dioxide, and air over heated salt :—

$$4NaCl + 2H_2O + 2SO_2 + O_2 = 2Na_2SO_4 + 4HCl$$

Page 378.—If a spectroscope of sufficient dispersive power be employed, it is seen that there are really two yellow lines, lying close together.

Page 382.—About the constitution of these compounds also, there is considerable doubt. When heated (*vide* ammonium chloride, p. 385), their vapours are generally found to contain free ammonia and the respective acids, unless the latter undergo further dissociation. Hence some chemists prefer to consider these salts as molecular compounds of the type, $NH_3 \cdot HX'$. The similarity in crystalline form and chemical properties of the compounds of ammonia to those of potassium and sodium lead however to the hypothesis that the former possess a like structure to that of the latter compounds. This would be the case if the ammoniacal salts were represented by the general formula NH_4X', the compound radical, NH_4, being supposed to possess properties like those of the atom of an alkaline metal. In favour of this latter view may be urged the fact that $N \left\{ \begin{matrix} (CH_3)_2 \\ C_2H_5 \end{matrix} \right.$ and C_2H_5I unite in molecular proportions to form a compound identical with that obtained by the combination of $N \left\{ \begin{matrix} CH_3 \\ (C_2H_5)_2 \end{matrix} \right.$ with CH_3I, although different products should have resulted were these mere molecular compounds. Further, on treating a concentrated solution of ammonium chloride with sodium amalgam a new compound (*vide* page 188) is obtained, which resembles many metallic amalgams but is very unstable, rapidly decomposing into ammonia and hydrogen. These gases do not however dissolve separately, or even when mixed, when they are exposed to mercury. Hence they are *probably* held, in the amalgam, in the form of the unstable radical, NH_4.

Page 387 note (i.)—According to experiments recently described (1891) by de Bruyn, hydroxylamine has been obtained in the free condition by the decomposition of its chloride by sodium methylate. After separation from the biproducts, the hydroxylamine was conducted into an ice-cooled receiver in which it crystallized in long needles, which were odourless, melted at 33°, and when rapidly heated suddenly decomposed.

Page 387 note (ii.)—Preparation of Nessler's solution. Dissolve 7 gr. potassium iodide and 2·6 gr. mercuric chloride in separate portions of 60 c.c. of water each. Pour the latter into the former until the red precipitate begins to become permanent. Then add 32 gr. solid caustic potash, a little more mercuric chloride, make up to 200 c.c. with water, and allow to stand. (Wanklyn.)

Page 414.—Potassium magnesium chloride, or Carnallite, is generally employed instead of magnesium chloride, in the manufacture of magnesium. The crude metal is purified by distillation, and if a still purer product is required it can be obtained by distilling the metal a second time. The Patricroft Magnesium Company (near Manchester) have thus succeeded in casting ounce-ingots of this metal almost chemically pure. There is considerable difficulty in drawing magnesium into the form of wire. The best plan is to warm it until it softens, and then press it through small holes by hydraulic pressure. Ribbons are produced by flattening the wires.

Page 417.—If the precipitation is carried on at the boiling temperature, the product is more dense ('magnesia alba ponderosa') than that resulting from precipitation in the cold, though the precipitate formed in the latter case be subsequently boiled ('magnesia alba levis').

Page 435.—Germanium (Ge.). Atomic weight, 72·3. An element, discovered in 1885 by Winkler in a silver-ore (argyrodite) found near Freiberg, has properties which place it between silicon (atomic weight, 28) and tin (atomic weight, 118), *i.e.* in the same group in Mendelejeff's table as zirconium.

It is a greyish-white lustrous metal, which melts at 900° and is only slightly volatilized at 1350°. At ordinary temperatures it is unaffected by air, but, when heated, forms the dioxide, GeO_2. Germanium forms also a monoxide, GeO, the corresponding sulphides, GeS_2 and GeS, tetrahaloid compounds, $GeCl_4$, (?)$GeBr_4$, GeI_4, and (?)GeF_4, and other compounds similar in type to those of silicon and tin.

Page 449.—The formula of ferric pyrophosphate is $Fe_43P_2O_7·9H_2O$, and that of the double salt is $Fe_43P_2O_7·2Na_4P_2O_7·7H_2O$.

Page 452.—The sesquisulphide is said to be formed by heating iron filings to dull redness in a current of sulphur-vapour.

Page 460.—Glatzel, in 1889, obtained manganese in a pure coherent condition by heating to redness, with magnesium dust, a mixture of manganous and potassium chlorides.

Page 473.—This unstable (chromic) acid is said to have been obtained, in the form of small red deliquescent crystals, by Moissan, by adding a little water to excess of pure chromic anhydride, maintaining the solution for some hours at 90°, and then decanting and cooling to 0°.

Page 476.—Some of the chromic acid is obtained in solution as calcium chromate. This is decomposed by adding a solution of potashes,

$$CaCrO_4 + K_2CO_3 = K_2CrO_4 + CaCO_3,$$

and the precipitated calcium carbonate filtered off.

Page 480.—The hydrate of a fourth oxide of uranium, $UO_4·2H_2O$, is precipitated, as a yellowish-white powder, by mixing a solution of a uranyl salt with hydroxyl.

Page 483.—In 1889 Krüss and Schmidt announced that they had discovered a new element, gnomium, to be present in small quantities both in nickel and cobalt; but subsequent experiments by Winkler and Fleitmann failed to confirm this statement. It is probable that the substance isolated by the two chemists first mentioned, was really a mixture of foreign metals present in the samples of nickel and cobalt examined.

Page 492.—Based upon this difference of behaviour between the salts of cobalt and nickel when boiled with excess of potassium cyanide, a method of separating these two metals has been devised. To the solution after prolonged treatment with the alkaline cyanide, an excess of a solution of sodium hypobromite is added, when nickel is precipitated as sesquioxide, but cobalt remains in solution.

When nickel which has been reduced from its oxides by treatment with hydrogen at 400° is allowed to cool in a slow stream of carbon monoxide gas, a volatile compound having the formula $Ni(CO)_4$ is formed. As cobalt does not enter into a similar combination with carbon monoxide, another method is thus offered for the separation of nickel from cobalt. (Mond, Langer, and Quincke, 1890.)

Page 502.—The sesquioxide, Pb_2O_3 or $2PbO{\cdot}PbO_2$, is obtained, as a reddish-yellow powder, by the action of a limited quantity of sodium hypochlorite upon a solution of a lead-salt. When treated with acids, it yields, like red-lead, the puce oxide and solutions of salts corresponding to the monoxide.

Page 533.—There is some doubt whether the mercurous salts are of the type $(Hg_2)''X'_2$ or $Hg'X'$. They unfortunately appear to undergo dissociation when volatilized, and hence their molecular weights cannot be fixed by determining their respective vapour-densities.

Page 549.—The precise nature of the change has not yet been determined; but the portion of the silvered film which is exposed to light evidently undergoes *some* modification which renders it more susceptible to the reducing action of the developer.

Page 555.—It is doubtful whether auric cyanide is known save in the form of double salts. The crystalline substance obtained by the action of hydrochloric acid upon silver-auric cyanide: $AgAuCy_4$, is probably auricyanhydric acid: $HAuCy_4+3H_2O$, which, on heating, loses water, hydrocyanic acid, and cyanogen, leaving aurous cyanide: AuCy, which, at a higher temperature, is also decomposed, so that metallic gold alone ultimately remains.

Page 566.—Such carbon compounds are generally termed amines: and it might be better to adopt a similar nomenclature for the ammoniacal compounds of platinum, using the term *diamine* however for the group $(NH_2-NH_3)''$. Thus, using the same numbers as are employed on page 564 to designate the same substances, they might be considered as:—

(i.) Platinosamine hydrochloride $Pt''\begin{cases}NH_2{\cdot}HCl\\NH_2{\cdot}HCl\end{cases}$

(ii.) Platinosodiamine hydrochloride $Pt''\begin{cases}(NH_2{\cdot}NH_3){\cdot}HCl\\(NH_2{\cdot}NH_3){\cdot}HCl\end{cases}$

and so on, similarly.

Page 567 note (i.)—From the diminution in the density of palladium by its union with hydrogen the specific gravity of solid hydrogen ('hydrogenium') has been calculated to be 0·62 at 15°; and, in a similar manner, its specific heat to be 5·7. The latter value approximates to that required for the fulfilment of Dulong and Petit's law as to the atomic heat of the elements.

(In connection with the remarks on page 567 concerning the metallic character of hydrogen, read also page 372.)

Page 567 note (ii.)—A hemi-oxide, Pd_2O, has also been described. It is produced by the direct action of oxygen upon the metal and is a dark-grey powder.

Page 570.—Osmous anhydride OsO_3 has not been isolated. When liberated by the addition of dilute nitric acid, from its compound K_2OsO_4, it decomposes into the dioxide and tetroxide:—

$$2OsO_3 = OsO_2 + OsO_4.$$

An osmium sesquioxide: Os_2O_3 has also been described. It is prepared by heating potassium osmochloride: $OsCl_3{\cdot}3KCl$, with potassium carbonate in a current of carbonic anhydride and is a black amorphous powder.

Page 577.—*Raoult's method of determining molecular weights.* From what has been said on page 577, it is evident that some other method than that based

upon Avogadro's law, is required for the determination of the molecular weights of substances which cannot be volatilized or which decompose when converted into the gaseous state. Now it is found that when a solid body is dissolved in a liquid, the freezing point of that solvent is depressed; and Raoult has shown that the depression of the freezing point of any solvent is, not only for any one substance directly proportional to the absolute weight dissolved, but that for compounds of similar nature, the depression is approximately inversely proportional to their respective molecular weights. Hence, *from a measurement of the lowering of the freezing point of a solution* containing a known percentage of any dissolved substance, x, the depression having been similarly determined for some substance of known molecular weight and of like nature, the molecular weight of x may be approximately determined.

TABLES.

I.—*Weights and Measures.*

1 lb. Avoirdupois	=	16 oz. Av.
	=	7,000 grains
1 oz. Avoirdupois	=	437·5 grains
1 lb. Troy	=	12 oz. Troy
	=	5760 grains
1 oz. Troy	=	480 grains
1 gallon	=	8 pints
	=	277·25 cubic inches
1 pint	=	20 fluid oz.
1 gallon of water at 62° F. (16°·7 C.) weighs		70,000 grains
1 cubic foot of water at 62° F. weighs		62·326 lb. Av.

1 metre (m.)	=	10 decimetres (dm.)
	=	100 centimetres (cm.)
	=	1000 millimetres (mm.)
	=	39·37 inches
1 foot	=	30·48 centimetres
1 inch	=	25·40 millimetres
1 litre (l.)	=	1000 cubic centimetres (c.c.)
	=	1·76 pints = 35 fluid oz.
1 pint	=	568 cubic centimetres
1 fluid oz.	=	28·4 ,,
1 kilogramme (kg.)	=	1,000 grammes (g.)
	=	2·205 lb. Av.
1 gramme	=	10 decigrammes (dg.)
	=	100 centigrammes (cg.)
	=	1000 milligrammes (mg.)
	=	15·432 grains
1 lb. Avoirdupois	=	453·6 grammes
1 oz. Avoirdupois	=	28·35 ,,
1 grain	=	64·8 milligrammes

II.—*Weight of one cubic centimetre of Dry Air in milligrammes at varying temperatures and pressures.*

(Temperature in ° C. and Pressure in mm. of Mercury.)

t	p=745	750	755	760	765	770	775
°							
0	1·268	1·276	1·285	1·293	1·301	1·310	1·319
1	1·264	1·271	1·280	1·288	1·296	1·305	1·314
2	1·259	1·267	1·275	1·283	1·292	1·300	1·310
3	1·254	1·262	1·271	1·279	1·287	1·296	1·305
4	1·250	1·258	1·266	1·275	1·283	1·291	1.300
5	1·245	1·253	1·261	1·270	1·2 8	1·286	1·295
6	1·240	1·248	1·256	1·265	1·273	1·281	1·290
7	1·236	1·244	1·252	1·261	1·269	1·277	1·286
8	1·232	1·240	1·248	1·256	1·264	1·273	1·282
9	1·228	1·236	1·244	1·252	1·260	1·268	1·277
10	1·223	1·231	1·239	1·247	1·255	1·263	1·272
11	1·219	1·227	1·235	1·243	1·251	1·259	1·268
12	1·215	1·223	1·231	1·239	1·247	1·255	1·263
13	1·210	1·218	1·226	1·234	1·242	1·250	1·259
14	1·206	1·214	1·222	1·230	1·238	1·246	1·254
15	1·202	1·210	1·218	1·226	1·234	1·242	1·250
16	1·198	1·206	1·214	1·222	1·230	1·238	1·246
17	1·194	1·202	1·210	1·218	1·226	1·234	1·242
18	1·189	1·197	1·205	1·213	1·221	1·229	1·237
19	1·185	1·193	1·201	1·209	1·217	1·225	1·233
20	1·181	1·189	1·197	1·205	1·213	1·221	1·229
21	1·177	1·185	1·193	1·201	1·209	1·217	1·225
22	1·173	1·181	1·189	1·197	1·205	1·213	1·221
23	1·169	1·176	1·184	1·192	1·200	1·208	1·216
24	1·165	1·172	1·180	1·188	1·196	1·204	1·212
25	1·161	1·168	1·176	1·184	1·192	1·200	1·208

III.—*Weight of one cubic centimetre and volume of one gramme of Water at varying temperatures.*

(Mean of Several Determinations.)

Temp.	Weight of 1 c.c. in grammes	Volume of 1 gr. in c.c.	Temp.	Weight of 1 c.c. in grammes	Volume of 1 gr. in c.c.
°			°		
0	0·999878	1·000122	13	0·999430	1·000570
1	0·999933	1·000067	14	0·999297	1·000703
2	0·999972	1·000028	15	0·999154	1·000847
3	0·999993	1·000007	16	0·999004	1·000997
4	1·000000	1·000000	17	0·998839	1·001162
5	0·999992	1·000008	18	0·998663	1·001339
6	0·999969	1·000031	19	0·998475	1·001527
7	0·999933	1·000067	20	0·998272	1·001731
8	0·999882	1·000118	21	0·998065	1·001939
9	0·999819	1·000181	22	0·997849	1·002156
10	0·999739	1·000261	23	0·997623	1·002383
11	0·999650	1·000350	24	0·997386	1·002621
12	0·999544	1·000456	25	0·997140	1·002868

IV.—*Pressure of Aqueous Vapours at varying temperatures.*

(Pressure in mm. of Mercury.)

Temp.	Pressure	Temp.	Pressure	Temp.	Pressure	Temp.	Pressure
°		°		°		°	
−15	1·44	+7	7·47	+17	14·40	+50	91·98
−10	2·15	8	7·99	18	15·33	60	148·88
−5	3·16	9	8·55	19	16·32	70	233·31
0	4·57	10	9·14	20	17·36	80	354·87
+1	4·91	11	9·77	21	18·47	90	525·47
2	5·27	12	10·43	22	19·63	100	760·00
3	5·66	13	11·14	23	20·86	110	1075·4
4	6·07	14	11·88	24	22·15	120	1491·3
5	6·51	15	12·67	25	23·52	130	2030·3
6	6·97	16	13·51	26	24·96	140	2717·6

V.—*Boiling-point of Water* (t) *under varying barometric pressure* (p).

p.	*t.*	*p.*	*t.*	*p.*	*t.*	*p.*	*t.*
	°		°		°		°
740	99.26	749	99·59	758	99·93	767	100·26
741	99·30	750	99·63	759	99·96	768	100·29
742	99·33	751	99·67	760	100·00	769	100·33
743	99·37	752	99·71	761	100·04	770	100·36
744	99·41	753	99·74	762	100·07	771	100·40
745	99·44	754	99·78	763	100·11	772	100·44
746	99·48	755	99·82	764	100·15	773	100·47
747	99·52	756	99·85	765	100·18	774	100·51
778	99·56	757	99·89	766	100·22	775	100·55

VI.—*Corrections to reduce the Readings of a Barometer with a Glass Scale at different temperatures to* 0°. (*Landolt and Börnstein.*)

(The Corrections are in mm., and are to be deducted from the Readings.)

Temp.	740 mm.	750 mm.	760 mm.	770 mm.	780 mm.
°					
1	0·13	0·13	0·13	0·13	0·13
2	0·26	0·26	0·26	0·27	0·27
3	0·38	0·39	0·39	0·40	0·40
4	0·51	0·52	0·53	0·54	0·54
5	0·64	0·65	0·66	0·67	0·67
6	0·77	0·78	0·79	0·80	0·81
7	0·90	0·91	0·92	0·93	0·94
8	1·02	1·04	1·05	1·07	1·08

VI.—*Continued.*

Temp. °	740 mm.	750 mm.	760 mm.	770 mm.	780 mm.
9	1·15	1·17	1·18	1·20	1·21
10	1·28	1·30	1·31	1·33	1·35
11	1·41	1·43	1·45	1·47	1·48
12	1·54	1·56	1 58	1·60	1·62
13	1·66	1·69	1·71	1·73	1·75
14	1·79	1·82	1·84	1·87	1·89
15	1·02	1·95	1·97	2·00	2·02
16	2·05	2·08	2·10	2·13	2·16
17	2·18	2·21	2·24	2·26	2·29
18	2·30	2·34	2·37	2·40	2·43
19	2·43	2·47	2·50	2·53	2·56
20	2·56	2·60	2·63	2·66	2·70
21	2·69	2·72	2·76	2·80	2·83
22	2·82	2·85	2·89	2·93	2·97
23	2·94	2·98	3·02	3·06	3·10
24	3·07	3·11	3·16	3·20	3·24
25	3·20	3·24	3·29	3·33	3·37

VII.—*Specific Gravity and Composition of Dilute and Concentrated Acids.*

Sulphuric Acid		Nitric Acid		Acetic Acid		Hydrochloric Acid	
Per cent. H_2SO_4 by weight	Specific gravity	Per cent. HNO_3 by weight	Specific gravity	Per cent. $HC_2H_3O_2$ by weight	Specific gravity	Per cent. HCl by weight	Specific gravity
5	1·031	5	1·030	5	1·0067	5	1·027
10	1·069	10	1·059	10	1·0142	10	1·050
15	1·106	15	1·089	15	1·0214	15	1·075
20	1·146	20	1·120	20	1·0284	20	1·101
25	1·184	25	1·153	25	1·0350	25	1·126
30	1·224	30	1·185	30	1·0412	30	1.151
35	1·266	35	1·218	35	1·0470	35	1·177
40	1·306	40	1·251	40	1·0523	40	1·200
45	1·351	45	1·284	45	1·0571	42·4	1·210
50	1·399	50	1·319	50	1·0615		
55	1·448	55	1·346	55	1·0653		
60	1·502	60	1·374	60	1 0685		
65	1·557	65	1·395	65	1·0712		
70	1·615	70	1·423	70	1·0733		
75	1·675	75	1·442	75	1·0746		
80	1.733	80	1·460	80	1·0748		
85	1·783	85	1·478	85	1·0739		
90	1·819	90	1·495	90	1·0713		
95	1·839	95	1·513	95	1·0660		
100	1·838	100	1·530	100	1·0553		

VIII.—*Specific Gravity and Composition of Alkaline Solutions.*

Caustic Potash		Caustic Soda		Ammonia	
Per cent. KOH by weight	Specific gravity	Per cent. NaOH by weight	Specific gravity	Per cent. NH_3 by weight	Specific gravity
5	1·041	5	1·058	5	0·979
10	1·083	10	1·115	10	0·959
15	1·128	15	1·170	15	0·941
20	1·177	20	1·225	20	0·925
25	1·230	25	1·279	25	0·911
30	1·288	30	1·332	30	0·898
35	1·349	35	1·384	33	0·891
40	1·412	40	1·437	36	0·884
45	1·475	45	1·488		
50	1·539	50	1·540		
55	1·604	55	1·591		
60	1·667	60	1·643		
65	1·729	65	1·695		
70	1·790	70	1·748		

To convert a density expressed in *Twaddell's* degrees into true specific gravity :—

Divide by 200 and add 1. Thus, 25° Twaddell $= \frac{25}{200} + 1 = 1{\cdot}125$.

IX.—*Heat of Formation and Solution of some Important Compounds.* (*After Thomsen.*)

NOTE.—The quantity of heat (H) is expressed in the number of kilogrammes of water which would be raised 1° C. in temperature on the formation of the molecular weight of the compound in grammes. Thus :—

$$(H^2, O) \;=\; +\;68{\cdot}4$$

means that on the formation of 18 grammes of water, or on the combustion of 2 grammes of hydrogen, the quantity of heat set free would raise 68·4 kilos. of water 1°. If heat is absorbed, instead of liberated, the number is expressed as a negative quantity.

Compound	H	Remarks
(H^2, O) . .	+ 68·4	Liquid water
$(H^2, O^2$, aq.) .	+ 45·3	Formation of H_2O_2 in dilute solution
(H^2, S) . .	+ 4·7	Gaseous H_2S
$(H^2S$, aq.) .	+ 4·6	Solution of H_2S in water
(H, Cl) . .	+ 22·0	Gaseous HCl
(HCl, aq.) .	+ 17·3	Solution of HCl in water
(H, Br) . .	+ 8·4	Gaseous HBr
(HBr, aq.) .	+ 19·9	Solution of HBr in water
(H, I) . .	− 6·0	Gaseous HI
(HI, aq.) . .	+ 10·2	Solution of HI in water
$(H, Cl, O^3$, aq.) .	+ 23·9	Formation of $HClO_3$ in dilute solution
$(H, Br, O^3$, aq.) .	+ 12·4	,, $HBrO_3$,,

IX.—*Continued.*

Compound	H	Remarks
$(H,I,O^3, aq.)$.	+ 55·8	Formation of HIO_3 in dilute solution
(S,O^2) . .	+ 71·1	Gaseous SO_2
$(SO^2, aq.)$. .	+ 7·7	Solution of SO_2 in water
(S,O^3) . .	+ 103·2	Liquid SO_3
$(SO^3, aq.)$. .	+ 39·2	Solution of SO_3 in much water
(H^2,S,O^4). .	+ 192·9	Liquid H_2SO_4
$(H^2SO^4, aq.)$.	+ 17·9	Solution of H_2SO_4 in much water
(N,H^3) . .	+ 11·9	Gaseous NH_3
$(NH^3, aq.)$.	+ 8·4	Solution of NH_3 in water
(N,H^4,Cl) .	+ 75·8	Solid NH_4Cl
(N^2,O) . .	− 17·5	Gaseous N_2O
(N,O) . .	− 21·6	Gaseous NO
$(H,N,O^2, aq.)$.	+ 30·8	Formation of HNO_2 in dilute solution
(N,O^2) . .	− 2·0	Gaseous NO_2
(H,N,O^3) . .	+ 41·6	Liquid HNO_3
$(HNO^3, aq.)$.	+ 7·5	Solution of HNO_3 in water
(P^2,O^5) . .	+ 369·9	Solid P_2O_5
(H^3,P,O^4). .	+ 302·6	Crystalline H_3PO_4
(P,Cl^5) . .	+ 105·0	Solid PCl_5
(P,Cl^3) . .	+ 75·3	Liquid PCl_3
(As,Cl^3) . .	+ 71·4	Liquid $AsCl_3$
(Sb,Cl^3) . .	+ 91·4	Liquid $SbCl_3$
(C,O) . .	+ 29·0	Gaseous CO from amorphous **C**
(C,O^2) . .	+ 97·0	,, CO_2 ,,
(C,H^4) . .	+ 21·8	Gaseous CH_4
(C^2,H^4) . .	− 2·7	,, C_2H_4
(C^2,H^2) . .	− 48·2	,, C_2H_2
(C^2N^2) . .	− 65·7	,, $(CN)_2$
$(K,Cl\ aq.)$.	+ 101·2	Formation of KCl in dilute solution
$(K,Br, aq.)$.	+ 90·2	,, KBr ,,
$(K,I, aq.)$.	+ 75·0	,, KI ,,
(K,Cl,O^3). .	+ 95·9	Crystalline $KClO_3$
(K^2SO^4) . .	+ 344·6	,, K_2SO_4
(K^2SO^4,H^2SO_4).	+ 16·6	Formation of $KHSO_4$ from K_2SO_4 and H_2SO_4
(K,N,O^3). .	+ 119·5	Crystalline KNO_3
$(KNO_3, aq.)$.	− 8·5	Solution of KNO_3 in water
$(Na,Cl, aq.)$.	+ 96·5	Formation of NaCl in dilute solution
$(Ca,Cl^2, aq.)$.	+ 187·2	,, $CaCl_2$,,
(Ca,C,O^3). .	+ 270·4	$CaCO_3$ as calcite
$(Ba,Cl^2, aq.)$.	+ 196·8	Formation of $BaCl_2$ in dilute solution
(Ba,SO^4) . .	+ 338·1	$BaSO_4$ as an amorphous powder
(Al^2Cl^6) . .	+ 322·0	Anhydrous Al_2Cl_6 (solid)
$(Al^2Cl^6, aq.)$.	+ 153·7	Solution of Al_2Cl_6 in water
$(Fe^2,Cl^6, aq.)$.	+ 255·4	Formation of Fe^2Cl^6 in dilute solution
$(Fe,Cl^2, aq.)$.	+ 100·0	,, $FeCl_2$,,
$(Zn,S,O^4, aq.)$.	+ 248·5	,, $ZnSO_4$
(Cu,O) . .	+ 37·2	Solid CuO
(Cu,S,O^4). .	+ 182·6	Anhydrous $CuSO_4$ (solid)
$(Cu,S,O^4, aq.)$.	+ 198·4	Formation of $CuSO_4$ in dilute solution
(Ag,Cl) . .	+ 29·4	Solid AgCl
(Ag,Br) . .	+ 22·7	,, AgBr
(Ag,I) . .	+ 13·8	,, AgI
$(Ag,N,O^3, aq.)$.	+ 23·3	Formation of $AgNO_3$ in dilute solution

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